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BAILEY'S  
ELEMENTARY CHEMISTRY

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"THE NEW MATRICULATION CHEMISTRY"

BY

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PRINCIPAL OF UNIVERSITY CORRESPONDENCE COLLEGE

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## PREFACE TO THE FOURTH EDITION.

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IN the first edition of this book considerable importance was attached to experimental methods of study. In the second edition this treatment was developed still further by the insertion of an Introductory Course designed both to train the student in scientific method, and to demonstrate to him the broad outlines and the leading principles of Chemical Theory

The work of preparing the fourth edition has been entrusted to Mr. H. W. Bausor, M. A., who has rewritten the Introductory Section in order to bring it into closer accord with the needs of beginners, and has made such further alterations throughout the remainder of the book as were deemed advisable.

An important distinction is made between the experiments by means of a difference in the size of type. Experiments which the student *himself* is intended to perform if opportunity allows are printed in small type, those printed in large type should be carried out by the teacher.

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# SECTION I.—INTRODUCTORY.

## CHAPTER I.

### PHYSICAL AND CHEMICAL CHANGES.

1. **The Method of Scientific Inquiry**—Let a person unacquainted with the aims and the conduct of scientific inquiry examine some material object, say a mineral, a piece of rock, or a pebble from the sea-shore, and let him then detail the points of interest which occur to him as the result of his examination. He may be struck by its form, its colour, its hardness, the nature of its surface, or he may be disposed to ask whence it came and how.

In what respects do his questionings differ from those of one trained in the methods of scientific investigation? In this, that the scientist is accustomed to grouping his observations, he is trained by experience to the recognition of likenesses and unlikenesses in such bodies so as to reject the trivial details, and hold firmly to the essential and characteristic ones

Investigation by a process of comparison and classification, however, opens up such a wide field, that it becomes necessary to proceed step by step, and press the inquiry along well-defined lines, each with a distinct purpose.

The geologist, desirous of determining the history of the strata, will devote himself to the observation of existing strata, their essential and prevailing characters, their

origin and mode of formation. The biologist, on the other hand, studies the structure of living organisms, classifying them according to their forms and functions, and tracing historically the occurrence and evolution of the different types. The physicist interests himself with the phenomena associated with matter, whilst the chemist deals with matter itself and its identification.

Now to all these, such objects as we have mentioned in the opening paragraph will appeal in a variety of ways. A piece of chalk, limestone, or marble are very different objects to the geologist, but may be much the same thing to the chemist if he finds them to be composed of the same kind of matter. A piece of glass rubbed briskly with silk becomes capable of attracting small light bodies, this observation is of little direct importance to the chemist if he finds that the substance of the glass has not changed or its mass become greater, though to the physicist such an observation may be of great significance. A piece of iron, so far as the chemist is concerned, retains its identity as iron whether it be in the form of a solid bar, the finest wire, or an impalpable powder, it may grow warmer and expand or by cooling contract; it may be endowed with the property of attracting other particles of iron or not, and yet its composition and mass may remain unchanged. So long as any modification of aspect or behaviour is such as experience has taught him belong to matter which he identifies as *iron* he maintains that no alteration in substance has taken place.

To sum up, we may say that the method of scientific inquiry as applied to Chemistry consists in experiment, observation and inference.

**2. Transmutation of Metals.**—The earlier chemists believed that they could change the baser metals into noble metals, quicksilver into gold or lead into silver, and most of their researches were pursued with this object in view. The more searching methods of inquiry adopted in later times have, however, shown that their conclusions were fallacious

So also, even to the time of Lavoisier, towards the close of the eighteenth century, chemists failed to realise what takes place when iron rusts or metals burn, although an actual change of substance has taken place, and matter is indeed added to the metals during the process.

These misunderstandings arose from two main sources :

(1) Failure to appreciate the *essential and characteristic* properties of the substance under consideration.

(2) Failure to test whether any *apparent* alteration of substance had been accompanied by increment or loss of substance during the experiment.

At each step the balance must be called upon to say whether any increment or loss of substance has taken place, and if so the source of this change in mass must be traced.

All conclusions, and especially those which form the foundation of further investigation, require to be fully and critically examined in order to see that the deductions drawn are justified by the facts.

**3. The Field of Inquiry for the Chemist.**—The aim of the chemist is then to investigate matter with a view to recognising and classifying the *essential* characters of each kind of matter, and to follow the changes which ensue whenever those changes involve a redistribution of matter.\*

Let us then follow the course of investigation by experiment, which will enable us to see how the information we require is to be obtained, and what deductions may be fairly made from the observations.

**Exp. 1. An apparent transmutation of iron into copper**—Into a solution of "blue vitriol" dip the bright blade of a penknife. After a short time remove the knife. Observe that the part of the blade which was immersed in the liquid has acquired the appearance of copper.

*Apparently* the iron of which the blade is composed has been changed into copper, and if you were to leave the investigation at this stage you might conclude that you had

\* Whether in the operations which he performs matter may be created or destroyed must for the present remain untouched. An appeal to his later observations must decide this.

succeeded in bringing about a transmutation of iron into copper. Not until you have carried out an exhaustive inquiry, and performed a series of somewhat complex experiments will you be in a position to decide what is the nature of the change you have observed. And this you are not in a position to undertake at present.

**4. The Nature of Physical and Chemical Change.**—At the outset of any inquiry relating to the science of chemistry it is necessary to acquire clear ideas as to the nature of chemical change and the distinction between this and physical change, and we shall find that in such an inquiry the use of the balance is indispensable.

**Exp. 2.**—Take the following objects:—

1. A small test-tube.
2. A porcelain crucible.
3. A few inches of platinum wire.

Weigh each of these carefully (seeing that they are quite dry and clean), and enter the weights in the column provided below, and also any notes descriptive of the objects. Now heat them for some minutes in the non-luminous flame of a Bunsen burner; observe the alterations which ensue during the heating, *e g* change of colour, softening, and enter these observations also in the table. In heating a crucible it will be desirable to support it on a pipe-clay triangle as shown in Fig 1.

Allow the objects to cool, and see how far they resume their original character. Weigh them when quite cold, and enter these results alongside the others.

Weight		Description as to Colour, Texture, etc.		
Before Heating	After cooling	Before Heating	During Heating.	After Cooling



**Exp 3.**—Now perform similar experiments with the following bodies, and make observations upon them in the same way, entering all your observations in tabular form.—

4. A fragment of sulphur in a test-tube.
5. A fragment of wax in a test-tube
6. A few crystals of iodine in a test-tube.

Carefully observe and note down any changes during the application of the heat, and also what takes place during the period of cooling. A pocket lens will be of assistance to you in some of your observations.

Do not press the heating so strongly as to drive vapours out of the mouth of the tube. [Find out, however, in the last example how it would affect the records you have made if you do so drive off vapours]

**Exp 4**—Heat for at least fifteen minutes in small porcelain crucibles, and record your observations in the same way:

7. Some small pieces of magnesium foil (with crucible cover loosely on).
8. Some small pieces of tin (without cover).
9. „ „ wood (without cover).

Having now before you the records of all your observations arranged in an orderly manner, you will notice that in the examples given you may collect them, *i. e.* generalise them, under the following heads:

(a) Those cases (1-6) in which there is no substantial\* alteration of weight, and in which, though whilst the heat was being applied changes of colour, etc., may have been evident, yet on cooling, the substance had, so far as we can judge, returned to its original form and character.

While hot the test-tube softened, became out of shape, and gradually acquired a red colour, the porcelain crucible became red-hot, and the platinum wire white-hot and softer so that it could be more easily drawn asunder; but all three objects regained their original appearance on cooling, though the test-tube remained out of shape.

Again the sulphur and wax melted on heating but

\* It will be useful to consider how very small variations having no particular bearing on the inquiry may occur, and how precautions might be taken to eliminate them.

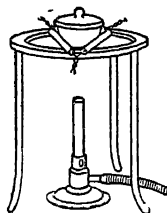


FIG. 1.

solidified on cooling, and then exactly resembled other fragments of the original substances; the iodine volatilised without melting, forming violet vapours, but when the test-tube was allowed to cool these vapours condensed on the sides of the tube in the form of blue-black crystals exactly like those originally taken.\*

(b) Those cases (7-9) in which alteration of weight (gain or loss) has taken place, and in which it will be observed that a distinct change in character and properties has been brought about

Thus the magnesium was converted into a very light fluffy white powder and the tin into a white powder,† in both cases with gain in weight, whilst the wood gradually burned away with loss of weight.

We thus recognise a striking difference in behaviour under the action of heat. Later on we shall examine more closely into the remarkable fact that substances often gain in weight under the action of heat, for it was this which led the earlier inquirers to the conclusion that heat was a ponderable substance, and that the increase in weight was due to the addition of matter which they called "caloric" to the body which was exposed to it.

For the present, however, let us confine our attention to the cases under Exps. 2 and 3. in which no alteration of weight has been found to take place and no permanent alteration of properties.

Many familiar examples of this class of phenomena will readily occur to you. Water is well known by its appearance and character, and is presented to us commonly as rain, or collected in rivers and in the sea. In the depth of winter, however, we see it become transformed into solid ice or snow, and later changing once more into water. The inhabitant of the Arctic regions is more familiar with it as ice, and the liquid water is to him a rarity. In tropical regions the reverse is the case, ice or snow being seldom seen. Yet we can readily satisfy ourselves with the aid

\* This phenomenon (of volatilising without melting) exhibited by iodine on heating is called *sublimation*.

† Reserve these powders for a later experiment.

of the balance, that ice passes into water or water into ice without change in weight or substance. And, similarly, we may examine the relation between steam or water vapour and water itself.

In the solid form it is ice or snow, in the liquid form it is water, in the gaseous form it is steam or vapour. The matter is the same, the form of its occurrence is different. That matter may exist in solid, liquid or gaseous forms and yet be in substance the same is not the exception but the rule. The difference of character is a difference of *physical state*.

Whether the substance is present to us as ice, or water, or vapour, depends on the *physical conditions* which prevail, and we realise by ordinary experience that *temperature* is the controlling factor. Yet ice may be transformed into water by *pressure* alone, or by sprinkling it with common salt.

**Exp. 5** — Make a mixture of three parts by weight of snow or crushed ice and one part by weight of common salt. Stir it well together until the ice or snow is nearly all melted. Now dip into the mixture the bulb of a thermometer, and note how the quicksilver shrinks (record the lowest reading of the thermometer).

Transfer the thermometer to hot water and see how the quicksilver increases in volume, occupying a greater space than it did before. Weigh the (dried) thermometer before and after one of these operations, and show that there is no change in the mass of the glass (which also contracts and expands) and quicksilver of which the thermometer is made.

**Exp. 6.** — Fit a small dry flask with an india-rubber cork and glass tube of the form shown in Fig. 2, and let it dip into a vessel containing liquid. Now place the flask in the mixture of ice and salt and afterwards in hot water, and note how the air in the flask contracts or expands just as the quicksilver did, but in greater degree.

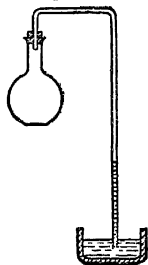


FIG. 2.

Summarising the results which these and similar observations bring home to us we find :—

(1) That matter may change in form (expand or contract), it may change in state (gaseous, liquid, solid), it may change in character (an impalpable powder, a crystalline

solid), or it may become softer or more brittle, porous or more dense, without any alteration of mass or variation of substance.

Such temporary modifications of character are classed as *physical changes*

(2) That matter may undergo modifications in the properties which it exhibits in response to the communication from without of heat, light, electricity, which are capable of being stored up by it, but which are imponderable, and therefore likewise bring about no alteration of mass.

Such properties are termed *physical properties*.

On the other hand the permanent modifications of character which matter undergoes when its mass is altered (as in Exp. 4) are classed as *chemical changes*, and those properties of matter which it exhibits when it undergoes chemical change are termed *chemical properties*.

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### QUESTIONS.—CHAPTER I.

1. Briefly explain what you understand to be the *method of scientific inquiry*
2. To what chief causes were the mistakes of the early chemists due?
3. What do you consider to be the field of inquiry for the chemist?
4. Describe an experiment illustrating the apparent transmutation of one metal into another.
5. Explain the difference between a *physical* and a *chemical* change.

## CHAPTER II.

### THE NATURE AND ACTION OF AIR.

**5. Operations of Weighing.—Effect of Moisture.**—Now let us make further inquiry into the results comprised under Exp 4 in the previous chapter, with the view especially of learning the significance of the changes in mass which have there been recorded.

The operations of weighing must now be performed in such a manner as to secure accuracy, and exclude the complications arising from causes really external to the experiment. Vessels, and especially finely-divided substances, if left about, take up moisture from the surrounding air, and become heavier, sometimes in a marked degree. We shall simplify our labours if we proceed in such a manner as to prevent this occurring.

This we can do by keeping the air of the balance case as dry as possible, and by providing a dry air chamber in which to keep the vessel and substance while it is cooling, for it must never be weighed until it is quite cold. The piece of apparatus shown in Fig 3 is termed a *desiccator*.

It is divided into two compartments communicating with one another. A circular piece of wire gauze is placed at the bottom of the upper compartment, and on this stands a pipe-clay triangle with the wires bent down to form legs;

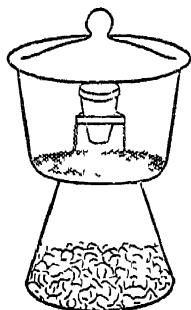


FIG 3.

crucibles, etc., can be supported on the triangle while cooling. The lower compartment contains calcium chloride, by means of which the air in the desiccator is kept dry.\*

**Exp 7** —Take a small porcelain crucible and half fill it with finely powdered sand or dried soil. Heat it over the Bunsen burner for say fifteen minutes, till it is red-hot throughout. Now remove it at once, while still hot, to the desiccator, and allow it to cool. Weigh it as quickly as possible. Leave it in the air of the room for a day, and then weigh it again. Note the increase in weight.

We shall henceforward take it for granted that wherever accuracy is desired such precautions will be adopted in order to exclude moisture.

### 6. Effect of the Presence of Air —

**Exp 8** —Introduce a small piece of lead into a porcelain crucible and weigh the whole. Heat over the flame of a Bunsen burner, and from time to time incline the crucible, turning it round so as to expose the bright surface of the metal. Continue the heating until there is no longer any bright metal to be seen, but in place of it a yellow substance, readily crushed and powdered. Cool and weigh. You will note that there is an increase in weight.

**Exp 9.**—Introduce lead into a crucible as before, and then fill up with clean white sand †; weigh; heat as before without disturbing the crucible or the sand overlying the lead. After say half an hour allow it to cool, and weigh. Note that there is no change in weight. Now throw out the sand and examine the lead at the bottom of the crucible. You will find that it has undergone no change except that it has melted and solidified again. Also examine the sand and note that its appearance has not changed.

A similar pair of experiments may be made using magnesium, tin, copper, or iron instead of the lead.

In each case you will find that under the conditions of Exp. 8 the metal undergoes a permanent change in character and increases in weight, whereas under the conditions of Exp. 9 there is no permanent alteration in character and no change in weight.

\* Leave a fragment of calcium chloride on a watch glass in the air of the room, and note how in the course of the day it becomes moist and increases in weight.

† The sand should have been previously strongly heated and allowed to cool in the desiccator.

**Exp 10**—Introduce a piece of charcoal into an open crucible and weigh. Now heat the crucible and observe that soon the charcoal glows and gradually burns away, leaving only a minute quantity of white ash.

**Exp 11**—Repeat the experiment, as with the lead, covering the charcoal with a thick layer of sand. Satisfy yourself that heating, even if continued for a considerable time, fails to bring about any material alteration in the weight. Now allow the crucible to cool and turn out the contents. You will find that neither the charcoal nor the sand has undergone any change.

**7 Review of the Experimental Results.**—From these experiments it appears that the transformation of lead into a yellow substance, differing in mass and in properties from lead, takes place under the conditions of Exp. 8, but not under those of Exp. 9. Likewise that charcoal burns away under the conditions of Exp. 10, and not under those of Exp. 11.

In what do these conditions differ? Chemists in the seventeenth century were fully aware of these changes, and were even aware of the fact that they were accompanied by a gain (or *apparently* in some cases a loss) of mass. The increment of substance was, however, regarded for long as of small importance, and attributed to particles derived from the flame.

In these experiments the flame and the heat are provided under both sets of conditions, and the sole difference that can be detected is that in one case there is free access of air, whilst in the other the substance is imprisoned beneath the sand and shut off from the air.

**8. Action of Air during the Heating Operation.**—Before we proceed to examine how and why the air effects such a change, let us satisfy ourselves that the lead, however unlikely it may appear to be so, is still contained in the yellowish residue from Exp. 8.

**Exp 12.**—Scrape out of the crucible some of this residue, powder it very fine, and introduce it into a fresh crucible. Now take about a gramme of finely-powdered charcoal, and mix it (by stirring with a thin glass rod) intimately with the yellowish powder. By gently tapping the crucible shake the contents well together, and cover the surface with a layer of powdered charcoal. Put a lid on the crucible.

[Why?] Heat over the flame for an hour without disturbance. Allow to cool, and then carefully shake out the charcoal and see what lies under it.

Examine the substance, press it in a mortar, and satisfy yourself that it corresponds to the metal taken in Exp. 10.

The suggestion which these experiments give rise to, that air plays an important part in the changes observed, is one that must be tested with great care, and further experiments must be devised in order more fully to appreciate the nature of the changes. For the present you will be satisfied to note, that while heating in air transformed the lead into a yellow powder with increase in mass, the heating of this yellow powder with charcoal has brought it back to metallic lead again.

**9. The changes which Air may effect at Ordinary Temperatures.—Rusting of Iron.**—Our next investigations will be made upon *iron*, a substance which possesses the advantages of being familiar to us, not only in itself but in the changes which it undergoes, and also in respect of the fact that such changes take place at ordinary temperatures.

**Exp. 13** —Obtain some bright iron or steel filings,\* sprinkle a thin layer of them on a watch glass; weigh; place in the desiccator, and leave them there for two or three days, after which again weigh. You will find that the weight remains unaltered. Examine the filings with a lens; they present the same appearance as at first.

**Exp. 14.**—Perform the same operations with the difference that the filings are left under a bell-jar, the inner surface of which is well moistened with water. This time you will find that there is an increase in weight and that the filings have become covered more or less completely with a reddish-yellow powdery-looking substance.†

The change which has taken place in the one case, and of which evidence is wanting in the other, is one that you must frequently have observed in iron utensils, railway lines, etc. It is termed “rusting,” and the reddish-yellow powder formed is called “rust.” So far you find it to be

\* Such filings are usually contaminated with oil, and this should be removed by shaking them with a little *ether*, pouring off the liquid, and then leaving them a few minutes in a dry, warm place—in a steam bath or in a gently warmed basin.

† Reserve these rusty filings for a later experiment.



associated with an increase in weight and apparently due in some way to the moisture, for in dry air it did not take place. Let us now try to find out whether rusting will take place in the presence of *moisture alone*.

**Exp 15.**—Fit a round-bottomed flask of about a litre capacity with a rubber cork, through which passes a short length of rather wide glass tubing to which is attached an inch or two of india-rubber tubing. Introduce about 300 c.c. of hot water, and drop into this some yards of bright iron wire wrapped into small compass by winding it round the fingers. Now boil the water, not too violently, but so that the steam issues freely from the end of the rubber tubing. Continue the boiling for at least a quarter of an hour, and then slip over the rubber tubing a strong brass clip, being careful, *just the instant before doing so*, to remove the burner. During the boiling the steam will have displaced the air almost completely from the flask. By turning the flask about you will be able to expose the wire to the space occupied by water vapour. Leave it so for some days, and note that the wire keeps quite untarnished. After that let in air, and notice how after some hours reddish-yellow rust forms on the wire.

*The rusting of the iron therefore takes place only in presence of air and moisture, and does not occur either in dry air or moisture alone.*

### 10. Does all the Air take part in the Process?

**Exp 16**—Take now a tall narrow cylinder moistened over its inner surface, and sprinkle iron filings freely over this surface. Invert over water contained in an earthenware or glass trough, taking care that you do not let any air escape from the cylinder. Note that soon the water begins to rise in the cylinder, and that after a day or two it rises no further. The air in the cylinder is now under diminished pressure. To restore the pressure to that of the atmosphere pour water into the trough till the level is the same inside and outside the cylinder. Mark the level carefully by means of a piece of gummed paper. Now remove the cylinder, empty it, and pour water into it from a graduated cylinder, noting the volume of water needed—

(a) To fill up to the mark

(b) To fill it from the mark to the top

You will find that the ratio  $a : b$  is approximately 4 : 1.

Repeat the experiment, and if in the first experiment none of the filings remained bright after the water had ceased to rise, use a quantity sufficiently large for this to be the case. You will find that the result is the same.

Obviously then only about one-fifth of the air takes part in the process of rusting, for some of the filings remain bright after this quantity has been removed.

11. What has become of the Air which has disappeared?—Recalling the fact demonstrated in Exp. 14 that the rusting of iron is accompanied by an increase in weight,\* we are justified in concluding that the air which has disappeared has become in some way fixed or added on to the iron, and that the result of this fixation is the conversion of the iron into reddish-yellow rust.

12. The Nature of the Change which takes place when Metals are heated in Air.—We have seen in Exps. 4 and 8 that when metals are heated in air they increase in weight and become changed into earthy-looking powders (which the early chemists called “calces” [sing. “calx”] of the metals). Can we explain these changes as we did the rusting of iron? If so, then they should be accompanied by the disappearance of a certain amount of air. Let us test this by burning magnesium (for example) in an enclosed volume of air.

Exp 17—Arrange a bell-jar in a trough containing water (see Fig 4). Let the bell-jar be ground on the base, and be not too narrow nor too large. If the trough be a glass one, it will be necessary to have a thin disc of rubber on the bottom upon which to press the bell jar firmly and so prevent any escape of air through expansion by the heat of combustion. Mark the level of the water in the jar by means of a piece of gummed paper. Attach a piece of magnesium ribbon to a cork which fits the bell-jar well. Ignite the magnesium, and *as quickly as possible* place it in the bell-jar, pressing down the bell-jar firmly with the other hand, and pushing in the cork tight. After burning brightly a short time the magnesium goes out.

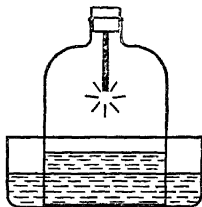


FIG. 4.

The water rises rapidly inside the jar. When it ceases to rise further pour water into the trough till the level is the same in bell-jar and trough. Again mark the level of the water with gummed paper. Now proceed, as in Exp 16, to measure the volume up to each gummed mark. The larger volume (say  $v$ ) represents the volume of air originally present in the jar; the difference between the two (say  $v - v_1$ ) the volume of air which has disappeared. You will find that  $v - v_1 : v = 1 : 5$ , i. e. one-fifth of the air has disappeared as in Exp 16.

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\* It is assumed that the student is acquainted with the fact that *air has weight*.

Similar results would be obtained by heating other metals in an enclosed volume of air, so that we may safely conclude that the change in appearance and properties and the increase in weight which the metals undergo is due to the fixation of air on them.

**Exp 18** —Allow some iron to rust in a cylinder of air, as in Exp 16, till the level of water ceases to rise. Place a glass plate over the mouth of the cylinder, take it out of the water and stand it upright on the table. Remove the glass plate and introduce a lighted taper; it is extinguished. Next burn magnesium in a bell-jar, as in Exp 17. Now take the cork out of the jar and introduce a lighted taper, again it is extinguished.

From this similarity in behaviour, and from the fact that in both Exps. 16 and 17 about one-fifth of the air was removed, we may suppose that ordinary air consists of two gases in the proportion of 4 : 1 by volume, and that iron on rusting and magnesium on burning have removed the constituent present in smaller quantity. This we may term the *active constituent*, and that present in larger quantity the *inactive constituent*. The latter has been named *Nitrogen*, and we shall in future call it by that name.

**13 Burning of Non-metallic Substances in Air** —Metals are, however, not the only substances which will remove the active constituent from air, any substance which will burn in air is capable of doing this, *e.g.* phosphorus, sulphur, a candle. Let us demonstrate this in the case of the first-named substance.

**Exp 19.**—Stand a small porcelain crucible containing some red phosphorus on a cork, and float on water in a trough. Place a large bell-jar with a narrow neck over the crucible. Mark the level of the water in the jar with gummed paper. Now ignite the phosphorus by touching it with a hot wire, and close the bell-jar *at once* by means of a cork or stopper. The phosphorus will burn brightly at first, and the heat evolved will expand the gas and depress the water inside the jar. After a little time the combustion will cease, and the water will ultimately rise above its original level. The fine white powder which is formed during the combustion (consisting of phosphorus pentoxide) will gradually settle down, and dissolve in the water. When the water has ceased to rise within the jar, pour more water into the vessel in which it stands until the level is the same in both. You will find (using the method of Exp 16) that *one-fifth of the air has disappeared*. Test the residual gas as in Exp. 18. It is nitrogen.

*Note* —Burn away all the remains of phosphorus in the crucible in a fume cupboard; *do not wipe it off with a cloth.*

14. The Active Constituent of Air (Oxygen).—We must now inquire whether it is possible to recover the active constituent of the air from the calx of a metal.

We choose for our first experiment a calx of mercury known as “red precipitate,” and which can be obtained by heating mercury for a long time at a certain temperature in contact with air.\*

**Exp 20** —Into a hard-glass tube introduce sufficient crystalline red precipitate to cover a threepenny-piece, and hold it in a Bunsen flame. Notice that the colour of the powder changes from scarlet to black—it looks “burnt” Take the tube from the flame, let it cool, and notice what happens. The scarlet colour is recovered. Evidently the change is not due to *burning*

Have by you a splinter of wood long enough to reach down to the bottom of the tube. Now heat the latter in the hottest part of the flame (*i.e.* near the tip). You will observe a mirror gradually forming on the sides of the tube. Ignite the splinter, blow out the flame, and thrust the glowing end down the tube. Observe that the glowing splinter bursts into flame, and burns more brightly than in common air.

Now scrape off the mirror formed in the tube with the clean end of the splint. You obtain a liquid metallic globule of “quicksilver” or *mercury*

If, then, mercury is heated in air to a certain temperature, we obtain the calx of the metal, and we have just found that, by heating the calx to a *higher temperature* (for the temperature of the hottest part of the Bunsen flame is much higher than that at which mercury is converted into red precipitate), the calx has been broken up again into mercury and a gas which is more active than ordinary air. This gas must, therefore, be the active constituent of air. It is called *oxygen*.

**Exp. 20 (continued)** —Try the same experiment, using red lead. Here, again, you obtain oxygen; *but the residue in the tube is not metallic lead*: it is a yellow solid, litharge, which is the *yellow* calx of lead, that is, the substance obtained in Exp 8 by heating lead in air [Red lead is also obtained by heating lead in air, but a lower temperature must be used than in the preparation of litharge.]

Now heat in a similar way the white powders you obtained from magnesium and tin in Exp 4, and the rusty iron filings formed in Exp 14. None of these gives off any oxygen.

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\* Red precipitate is usually prepared by quite a different method, and is a substance which may be easily procured from the chemist.

It is clear, therefore, that the oxygen is not recoverable from *all* the bodies obtained by heating metals in the air or simply exposing them to the air, as in the case of iron rust—at any rate, not by simple heating

15. **Elements and Compounds**—Red precipitate contains, then, at least two substances—mercury and oxygen—which are joined together in some mysterious way, so that the product is an entirely different substance from either of its constituents. This kind of union is termed *chemical combination*, and both the formation of this substance by heating mercury in air and its subsequent decomposition by heat are excellent examples of *chemical changes*. Red precipitate is an instance of a chemical compound; so also are red lead, iron rust, and the calces of the metals in general. Chemical compounds, then, are evidently substances which may be split up into two (or more) new substances. Now neither mercury nor oxygen has, so far, by any means in the chemist's power, been decomposed into anything simpler. Substances like mercury and oxygen, which have up to the present resisted all attempts to break them up into simpler bodies, are termed **elements**. Nitrogen is also an element, as are all the pure metals, as well as sulphur, carbon, and a great many substances. In all about 75 elements are known; but some of them are very rare, and only obtained with great difficulty.

A chemical compound containing oxygen and some other element is termed an *oxide*: red precipitate, for instance, is *oxide of mercury*; red lead and litharge are *oxides of lead*; iron rust is an *oxide of iron*.\*

16. **Preparation of Oxygen in Quantity**.—We have seen that it is not easy to obtain supplies of pure oxygen, unmixed with other gases, from the atmosphere; nor are there naturally occurring substances which readily yield the gas in quantity. "Nitre," which is found in quantity in Chili, and "pyrolusite" (manganese dioxide) will, when *strongly* heated, give up fire-air, and were used by the earlier chemists as sources of the gas.

\* It is not, however, pure oxide of iron, in addition it contains ferric hydroxide and ferrous carbonate in varying proportions.

There are, however, substances which have been specially prepared by the chemist more convenient for the purpose than red precipitate, or red lead, or any of these naturally occurring bodies. One of these is "chlorate of potash," the nature of which you will more fully appreciate at a later stage. We shall use it at present merely as a means of obtaining oxygen free from other gases.

**Exp 21.**—Heat a small quantity of potassium chlorate in a test-tube. Notice that it first crackles, then melts, and at last seems to boil. At this stage test the issuing gas with a glowing splinter. It will be found to be oxygen. Now heat some more potassium chlorate, first grinding it up in a mortar with a little manganese dioxide, till the substances are thoroughly mixed. Observe that the mixture gives off oxygen much more readily than potassium chlorate alone.

It is a remarkable fact that the manganese dioxide is unchanged at the end of the operation, the oxygen appearing to have come from the chlorate only. It is, however, very likely that the manganese dioxide does take some part in the reaction, but we cannot stop to discuss the question here.

The mixture just described is the one generally used to prepare oxygen in large quantities, and is often called the "oxygen mixture."

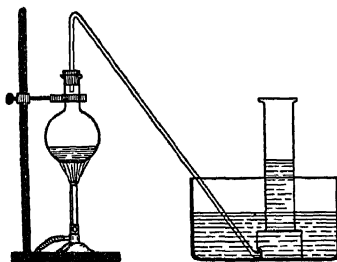


FIG. 5.

**Exp. 22** —Bend a glass tube, about a foot in length, into the shape shown in Fig. 5, and pass the longer end through a cork fitting into a round-bottomed flask of hard glass.

Pour sufficient water into a pneumatic trough to cover its shelf by at least half-an-inch. Fill one large gas-jar and five smaller ones with water and invert them in the trough. Have ready some ground-glass covers to be placed over the mouths of the jars when filled with gas.

Fill the flask about one-quarter full with a mixture of potassium chlorate with about one-quarter of its weight of manganese dioxide, and fix it as shown in the figure, so that the delivery tube just dips under the shelf of the trough. Use a small flame to heat the mixture, and move it to and fro to avoid getting too high a temperature. Oxygen soon comes off rapidly, and after allowing a short time for the air in the flask to be driven out, place a jar in position on the shelf, and, when filled, quickly cover its mouth while still under water with a glass plate, and replace it by a second jar, and so on.

We have collected the oxygen by the “displacement of water,” a method generally employed for collecting gases that are not too soluble in water.

*-Note on Manganese Dioxide.*—Before using a fresh sample of this compound for the production of oxygen, it should always be tested for carbonaceous matter (soot, etc.), as such material is apt to cause explosion when heated with potassium chlorate. To do this, mix it with some of the chlorate and heat gently in an open crucible. If the action is violent, reject the sample of dioxide.

## 17. Properties of Oxygen and Comparison with Ordinary Air.—

**Exp 23**—You will already have noticed that oxygen is colourless like ordinary air. Remove the cover from a small jar of the gas and inhale a little of it. You will find that it is odourless and tasteless, but that it produces a feeling of exhilaration as though it were ordinary air *intensified*.

**Exp 24**—Fill the bowls of two deflagrating spoons (see Fig. 6) with flowers of sulphur, ignite the sulphur and plunge one spoon into a jar of air, the other into a small jar of oxygen, taking care that the brass plates of the spoons fit down on the jars. Observe that in both cases the sulphur burns with a pale blue flame and gives off white fumes, and that on slightly raising the spoons the familiar disagreeable odour of burning sulphur is noticeable. The only difference you will observe is that in the case of oxygen the burning is more vigorous and the smell more intense.

*Note.*—Burn off all the sulphur remaining on the spoon before doing the next experiment.

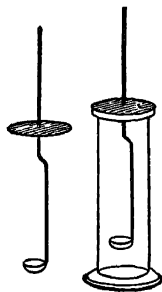


FIG. 6.

**Exp. 25.**—Cut off from some yellow phosphorus, *held below water*, a piece not bigger than a pea, and transfer it on the point of a knife to the clean, cold deflagrating spoon. Dry it by touching it with a bit of filter paper, and watch it for a few seconds. White fumes with a peculiar odour are given off; the phosphorus is already reacting with the air. Touch the phosphorus with a warm glass rod and plunge it into a jar of air, keeping the brass plate well down on the jar. Note that the phosphorus burns with a bright white flame evolving dense white fumes.

Repeat the experiment with a small jar of oxygen and observe that the result is the same, but that the flame is more brilliant.

*Note.*—Burn away all the remains of phosphorus on the spoon in a fume cupboard.

**Exp 26**—Wire a bit of charcoal to the end of a deflagrating spoon. Make it red-hot, then remove it from the flame and watch it. It soon ceases to glow. Now make it red-hot again and introduce it into a small jar of oxygen. It continues to glow and gradually disappears, just as it did in air when the external heating was kept up as in Exp 10.

**Exp 27.**—Attach a piece of magnesium ribbon to a deflagrating spoon, ignite the end of the ribbon and plunge it into a jar of air. Note that the magnesium burns with a very bright flame and formation of white fumes, which settle down as a white powder on the walls of the jar. Repeat the experiment with a small cylinder of oxygen. You will observe that the result is similar but that the burning is much more vigorous, the flames being intensely bright.

**Exp 28**—Introduce through a funnel sufficient sand to cover the bottom of the large jar of oxygen which you collected to a depth of about half-an-inch. Roll 8 or 10 inches of thin iron wire round a glass rod to form a spiral, and fasten a bit of match stalk to one end. Attach the other end to a deflagrating spoon. Light the match and plunge the wire into the jar. The iron wire burns and small black globules fall on to the sand. Repeat this experiment, using a cylinder of air; the wire does not burn.

It is quite obvious from the foregoing experiments that oxygen possesses the properties of ordinary air in an intensified degree, or in other words that air behaves as though it were diluted oxygen. We shall experience no difficulty in understanding this when we recall the fact that only one-fifth of the air is oxygen, the remainder consisting of the inactive gas nitrogen.

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## QUESTIONS.—CHAPTER II.

1. Describe a *desiccator* and explain its use.
2. Describe two experiments illustrating the part played by air in chemical changes.
3. What conditions are necessary for the rusting of iron? Describe experiments in support of your answer.
4. What do you suppose takes place when magnesium burns in air? Describe the experiments you would perform to verify your statement.
5. What is red precipitate? What happens when it is heated? What other red powder behaves somewhat similarly? In what respects do they differ?
6. Distinguish between "element" and "compound." Give as many examples as you can of substances belonging to each of these classes of bodies.
7. How would you prepare oxygen gas in quantity? Sketch the apparatus you would use. Describe in detail the experiments you would perform to show that when substances are burnt in oxygen the products are the same as when the same substances are burnt in air.
8. Describe as carefully as you can how you would prove that when phosphorus burns in air in a confined space one-fifth of the air disappears. What has become of this portion? Why is it necessary to make the level of the water inside and outside the jar the same before measuring the residual volume of air?

## CHAPTER III.

### THE NATURE AND ACTION OF WATER.

18. **Behaviour of Substances towards Water.**—We will commence our study of water in a manner similar to that which we followed in the case of air, *i. e.* by investigating the changes which familiar substances undergo in contact with water. Let us take *nitre* or *saltpetre* (potassium nitrate) as our first substance.

**Exp 29**—In a test-tube containing a little cold water place a few crystals of nitre. Notice that they gradually get less and less in bulk, and finally disappear *from sight*. We say the nitre has dissolved, and that it is *soluble* in water. What we have in the test-tube now is a *solution of nitre in water*. The water is termed the *solvent*. The word *solute* has been suggested for the substance (in this case nitre) that has dissolved.

Now add more nitre, and shake; probably that will dissolve also. At length, however, if we continue to add the solid, a point will be reached at which some will remain undissolved in that quantity of water.

We have now a *saturated solution* of nitre in *cold* water. There are two ways in which we could cause the still undissolved portion to pass into solution: one is very obvious—namely, the addition of more water; the other, not so obvious, is by warming the water already there. The hot solution would dissolve more nitrate before the point of saturation was reached; but *this* also would, in the end, become saturated. We may obviously have saturated solutions at various temperatures, and it is evident that the quantity of solid necessary to produce such a solution will depend on two things at least—(1) the quantity of water present; (2) the temperature of that water.

**19. Crystallisation.**—If now the hot saturated solution be allowed to stand for some time, the nitre will reappear; it will separate out from the solution in the form of crystals, but only in part, for the remaining liquid must always be a saturated solution. These crystals will almost certainly be large and well formed, as crystals usually are when they form by the slow cooling of hot saturated solutions (or the slow evaporation of cold saturated solutions).

**Exp 29 (continued).**—Allow the hot solution of nitre to stand. Note the formation of crystals

If the hot solution be poured into a clock-glass, the crystals will be small and will separate more quickly, because the cooling is rapid owing to the large surface exposed. A crystal has a definite geometrical form, and many substances may be recognised by the shape of their crystals. The student should examine and draw well-formed crystals of calcite, alum, sugar, and blue vitriol. If a well-formed crystal of any substance be suspended by a very fine thread in a saturated solution of the same substance, it will grow at the expense of the solution, but will usually retain its shape. In this way very large and almost perfect crystals of some substances may be obtained. Alum is a good substance to experiment with in this way.

**Water of Crystallisation.**—Many crystals when heated give off water and fall to a powder. Blue vitriol, or copper sulphate, will serve to illustrate the peculiarity of some crystalline substances.

**Exp. 30.**—Grind up some crystals of copper sulphate to a fine powder. Introduce a little of the powder into a porcelain crucible and weigh (with lid). Place the lid so that it only partly covers the crucible, and heat over a small flame which does not touch the crucible. Notice that the powder gradually becomes white. Now place the lid completely on the crucible and remove to a desiccator. When cold weigh. You will find that there is a loss in weight.

Now drop a little water upon the powder (anhydrous\* copper sulphate) and note the return of the blue colour. This serves as a delicate test for the presence of water.

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\* From a Greek word meaning *without water*.

If the white powder is dissolved up again in water and partially evaporated, and then set aside to cool, blue crystals may again be obtained. Water appears to be essential to the formation of some crystals. Such water is termed *water of crystallisation*. Washing soda, alum, and borax contain also a large proportion of such water.

**Amorphous** substances are those which do not possess a crystalline form. Examples of this class are chalk, charcoal, and starch.

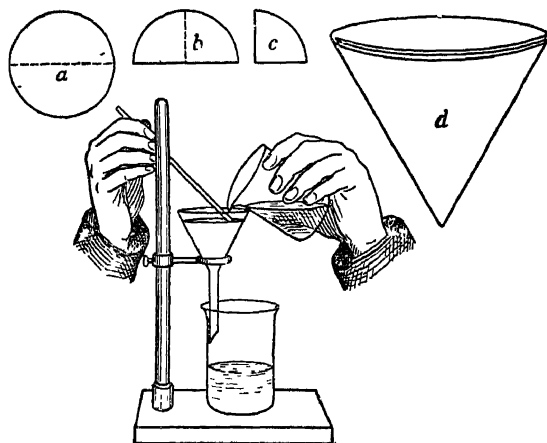


FIG. 7.—a, b, c, d indicate the manner of folding the circular filter paper.

## 20. Filtration.

**Exp 31**—Fit up a filter of the form shown in Fig 7, and pour through it some of the nitre solution obtained in Exp. 29 (using unglazed paper, called *filter paper*) You will find that the whole of it runs through. Nothing of a solid character is retained by the paper.

From this we gather that *dissolved matter cannot be removed by filtration*, the pores of the filter paper are evidently larger than the particles of the dissolved substance (as well as those of the solvent). To recover the *solute* (nitre in this case) we must either boil off the solvent (water) or allow it to evaporate into the air.

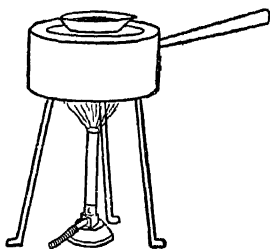


FIG. 8.

**Exp. 31 (continued).**—Pour some of the nitre solution into a porcelain dish and evaporate off the water by placing it on a water bath (see Fig. 8). The nitre remains behind.

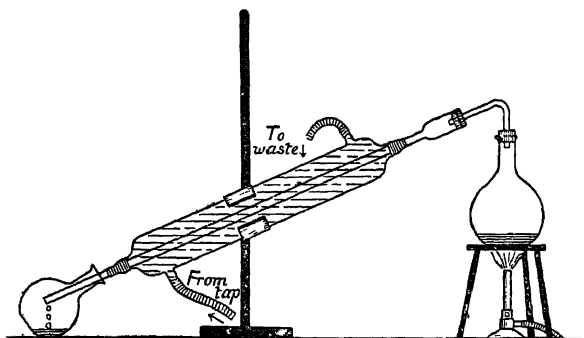


FIG. 9.

**Distillation.**—If we wish to recover the *solvent* (in this case water) we must make suitable arrangements to condense it. This is best done by using a *Liebig condenser*, which consists of a glass tube surrounded by a wider tube, through which cold water is made to circulate (Fig. 9).

**Exp 31 (continued).**—Pour the remainder of the nitre solution into a flask and connect with a condenser, as shown in Fig. 9. Boil

the liquid in the flask. The steam passes through the inner tube of the condenser, where it becomes liquid, and flows down into the flask placed to receive it. Do not boil off all the water or the flask may crack. Evaporate to dryness a little of the condensed liquid. There is no residue, shewing that only the water has passed over.

The process of boiling a liquid and condensing and collecting the vapour as you have done in Exp. 31 is known as *distillation*.

**21. Solubility Curves.**—Let us now investigate the solubility of nitre quantitatively at different temperatures.

**Exp. 32**—Introduce about 100 c.c.s of water into a small flask, add some finely powdered\* nitre, and shake well. If the powder all dissolves add more and shake again. Repeat the addition of nitre, if necessary, till some remains undissolved after vigorous shaking, *i. e.* the solution is *saturated*. Allow the mixture to settle, take the temperature of the liquid with a thermometer (say 10° C.), and then pour off about 10 c.c.s of the clear liquid into a weighed porcelain dish, after carefully wiping the inside of the neck of the flask, on which there may be some solid nitre, or water unsaturated with nitre. Weigh again. The difference gives the weight of the solution (*w* gms say).

Now evaporate to dryness on the water bath, wipe the moisture off the bottom of the dish, and weigh. The difference between this and the weight of the empty basin gives the weight of nitre dissolved.

Suppose this is  $w_1$  gms., then we have  $w_1$  gms of nitre dissolved in  $w - w_1$  gms of water. Therefore at 10° C. the weight of nitre which would dissolve in 100 gms. of water would be  $\frac{w_1}{w - w_1} \times 100$  gms. This is the *solubility of nitre at 10° C. expressed as a percentage*.

Now warm the water in the flask to about 20° C. and find the solubility as before. Repeat at 30°, 40°, and 50° C.

Next take a piece of squared paper and draw two lines (axes) at right angles, one horizontal along the bottom of the paper, the other vertical along the left-hand side.

Mark off along the horizontal axis lengths proportional to the temperatures taken, and on the vertical axis lengths proportional to the solubilities. Now from each point representing a solubility draw

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\* Solution takes place more rapidly and effectively if the substance is finely powdered.

a horizontal line till it cuts a vertical line from the corresponding temperature. Make a cross at the point of intersection. Join the centres of the crosses by a line, drawing the line so that it forms a smooth curve (see Fig 10). This is called the *solubility curve* of nitre.

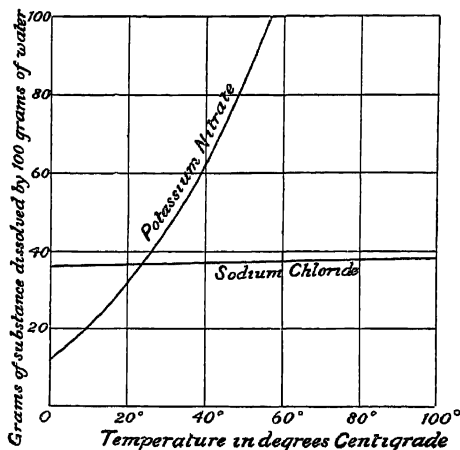


FIG. 10.

By means of this curve you can at once find the solubility of nitre at any temperature between 0° C. and 50° C. All you have to do is to follow the vertical line corresponding to the required temperature till it cuts the curve; then follow the horizontal line from this point till it cuts the vertical axis and read off the solubility.

Other examples of soluble substances are common salt, sugar, Epsom salts, bicarbonate of soda, alum and borax. You might construct solubility curves for them as you did for nitre. You would find that the solubilities of these substances vary greatly; also that whilst in some cases, *e.g.* nitre, the solubility increases very rapidly with rise in temperature, in other cases, *e.g.* common salt, the increase is very slight indeed.

**22. Other Solvents.**—It is important for the student to remember that water is not the only substance which possesses this property of dissolving solids. *All* liquids possess this power, in a greater or less degree, though any given liquid does not necessarily dissolve the same substances as another liquid.

Some substances that will not dissolve in water dissolve readily in other liquids. Sulphur, for example, is very soluble in a liquid called *carbon bisulphide*, and resin in *alcohol* or *methylated spirit*.\*

**Exp 33**—Powder a small piece of sulphur and introduce it into a little carbon bisulphide in a test-tube, a little at a time, and shake till completely dissolved. Then pour on to a clock-glass and allow the liquid to evaporate slowly (in a fume closet). Note the yellow crystals of sulphur which form.

### 23. Insoluble Substances.—

#### *Behaviour of Chalk towards Water.*—

**Exp. 34**—Shake up a quantity of chalk with distilled † water and allow the mixture to stand for a considerable time, the chalk settles down to the bottom, and leaves a clear liquid above. A quantity of this clear liquid may be poured off (*decanted*) without allowing any chalk to be carried with it. Substances which have a greater density than chalk (such as red lead) would subside sooner, and the liquid above could in those cases be more easily and completely separated from the solid.

This is the process known as *separation by decantation*. We could never by this means effect complete separation. We could, however, separate the chalk and water quite easily and completely by means of the filter described in § 20.

**Exp. 34 (continued).**—Pour the mixture of chalk and water on to a filter. The liquid portion which runs through the filter is termed the *filtrate*, and the chalk left on the paper is called the *residue*.

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\* These liquids are very volatile and inflammable, and should not be boiled in the open air, but in a distillation apparatus, on a water-bath. They may, however, be allowed to evaporate slowly in the open air, without the application of heat.

† *Distilled water* is water produced by boiling ordinary tap water and condensing the steam by a suitable cooling apparatus; on the small scale a Liebig condenser (see Fig 9) may be used for this purpose. Distilled water contains no dissolved solid matter.



It remains to be seen *whether the filtrate contains any chalk in solution*. To ascertain this, evaporate some to dryness on the water bath. *No residue is left*, hence we conclude that chalk does not dissolve in water.

The experiment should now be repeated with gypsum and slaked lime, and the results compared. Both these substances will be found to dissolve, but only to a slight extent.

Since the chalk is retained by the filter paper, it is evident that the pores of the paper are too small to allow the chalk particles to get through, but they cannot prevent the water passing through, nor were they small enough to prevent dissolved nitre going through with the water.

The residue on the filter paper may be dried by heating at some distance over a small Bunsen flame, or in a steam oven, and by this means recovered in its original form.

Substances which do not dissolve in water, but which when mixed with it, even in small quantity, can still be seen, are said to be *suspended* or *in suspension*. *Suspended matter* can always be *completely removed by filtration*, provided the filter paper is fine enough.

Sulphur, red lead, sand, charcoal, may be mentioned as other examples of bodies which are insoluble in water.

**24. Separation of Mixtures.**—It will not be difficult now for the student to see how we could effect a separation of two substances when one is soluble in some liquid and the other is not. It is only necessary to warm the mixture gently with an excess of the solvent, and filter. The insoluble portion remains on the filter, the soluble portion runs through and may be recovered as described already (by evaporation of the solvent). Chalk and nitre should now be mixed, and the substances separated in the way just described.

**Exp 35 —Separation and Isolation of the Constituents of Gunpowder.**—Using the knowledge already gained concerning soluble and insoluble substances, the student will find this also an instructive exercise. Gunpowder contains three ingredients—nitre, sulphur, and charcoal. Of these nitre is soluble in water; sulphur and charcoal are insoluble; but of these sulphur dissolves in carbon bisulphide.

To separate them we proceed as follows.—Shake the gunpowder with water, warm gently, and filter the filtrate contains the nitre, which can be recovered by evaporation of the water; wash the residue on the filter by pouring water over it a few times, then dry it carefully, scrape it off the paper and add carbon bisulphide. Shake and allow to stand, filter off the liquid from the black charcoal and let it evaporate slowly in a fume cupboard. The sulphur is thus recovered. The charcoal remains behind on the filter. It should be washed with a little carbon bisulphide to free it from adhering sulphur, and then dried.

**25. Water as a Solvent for Liquids**—Water dissolves not only many solids, but also some liquids as well. If alcohol is shaken up with water, the two liquids mix thoroughly, and no process of filtering will separate them. Every one, on the other hand, is familiar with the behaviour of oils towards water. Oils do not dissolve in water, but either float on the top or sink to the bottom, according as their density is less or greater than that of water. Partial separation may be effected in these cases by decantation; but for more complete separation we must have recourse to special apparatus (such as the separation funnel).

Carbon bisulphide, chloroform, and turpentine are other examples of liquids which do not dissolve in water: the first two, being denser, sink; the last-named, being lighter, floats on the water. Ether is an example of a liquid which is only slightly soluble in water; so that some would dissolve while the remainder would float on the water.

**26. Water as a Solvent for Gases.**—When a bottle of soda water is opened, bubbles are seen to rise in large quantities to the surface. When these bubbles have ceased coming off the liquid can be made to effervesce again by shaking the bottle. When shaking no longer produces effervescence, a further supply of bubbles can be liberated by warming the liquid. All this effervescence is due to the escape of *a gas that was dissolved in the water*. By means of a suitable arrangement this gas, which is carbon dioxide, can be collected.

Again, ordinary tap water contains gas dissolved in it.

This gas consists of air and carbon dioxide,\* it may be partially expelled on warming the water, and may be completely expelled on heating to the boiling point. Unlike solids, *gases dissolve better in cold water than hot*. The quantity of a gas dissolved in water will depend upon the pressure exerted by the gas upon the water, as well as upon the temperature of the water. The gas in soda water is forced in under pressure; when the pressure is relieved by taking out the stopper some of the gas escapes.

One litre of ordinary water at 15° is able to dissolve at the ordinary pressure about 16 c c of air.

Aquatic animals (fishes, etc.) obtain the air they breathe from that which is dissolved in the water in which they live.

Just as in the case of solids and liquids, some gases dissolve more readily than others. It is especially important to remember in some of the experiments that follow that water is able to take up gases if brought in contact with them.

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### QUESTIONS.—CHAPTER III.

1. Explain the terms *solvent*, *solution*, *water of crystallisation*, *saturated solution*. How would you separate and recover the ingredients in a mixture of powdered sulphur and common salt?
2. Describe carefully how you would proceed to ascertain whether a given white powder was soluble in water or not. How would you expect the following substances to behave when added to water.—Epsom salts, powdered charcoal, carbonate of soda?
3. Describe in detail how you would proceed to obtain pure water and pure nitre from a solution of nitre in water. Sketch the apparatus you would employ.

\* Tap water always contains a considerable quantity of carbonic acid gas derived from subterranean sources.

4. What do you understand by the term *solubility curve*?  
How would you proceed experimentally to obtain the solubility curve of washing soda between 15° C. and 70° C.?
5. How would you proceed to prove that alum is more soluble in hot than in cold water?
6. Explain what is meant by *distillation*, and describe an experiment to illustrate its use.
7. Describe how you would proceed to investigate the action of heat on blue vitriol. State and explain what you would observe.
8. If you were provided with a mixture of chalk and powdered borax, how would you proceed to obtain a pure dry specimen of each constituent?

## CHAPTER IV.

### THE NATURE AND ACTION OF WATER (*Continued*).

#### 27. Action of Water on Metals.—Production of Hydrogen.—

##### (a) *Sodium.*

**Exp. 36** —Take a piece of sodium about the size of a pea (*not larger*) and drop it into a small quantity of water contained in a beaker. Watch the behaviour of the metal through the *side* of the vessel, not over it, as the hissing globule sometimes explodes. A thin heavy stream may be seen falling from the disappearing metal. Is the metal simply dissolving in the water? It was angular when cast on the water: it is now globular, the solid has become liquid. Its temperature has probably risen. Had the metal been placed upon a floating filter paper, the temperature would have risen sufficiently to produce a flame. Chemical action between the metal and the water may therefore be suspected.

Fill a small gas-jar with water and invert it in a trough. Cut off a piece of sodium about the same size as the first, wrap it up in tin-foil or thin sheet lead perforated with a few pinholes, and place it under the gas-jar. Bubbles of gas are now seen to rise apparently from the metal. When bubbles cease to rise place a greased cover over the mouth of the jar and turn up the latter. Bring a lighted match near and slide the cover to one side. The gas burns with a yellow flame.

The inflammable gas is called **hydrogen**. The yellow colour of the flame is due to the sodium.

Rub the liquid in the beaker between your fingers. It is soapy. Taste it. It is *caustic*. Test it with red litmus paper.\* The colour changes to blue, *i. e.* the solution is *alkaline*. Evaporate the liquid to dryness in a porcelain dish. The residue is not sodium, which we should expect to find if the metal had merely dissolved in the water. The white solid is *caustic soda*, and is the same substance as that from which the solution labelled "sodium hydroxide" is made. Dilute a few drops of this liquid with water and apply the tests to it mentioned above.

### (b) Iron.

We have seen in Exp. 13 that water alone has no action on iron even at the boiling point.

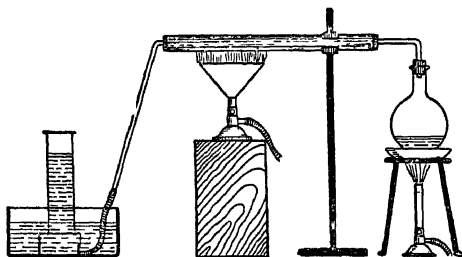


FIG 11.

Let us now try whether there is any action at a higher temperature, namely at a red heat.

Exp 37 — Fit up and arrange the apparatus shown in Fig. 11. It con-

sists of an iron tube a foot or more in length and a little over half-an-inch in diameter, partly filled with iron turnings or small nails. It is fitted properly at the ends with corks, one being pierced by a glass tube bent at right angles and passing into the flask containing a little water, while through the other projects the delivery

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\* *Litmus* is a vegetable colouring matter, which is very sensitive to the action of many chemical substances. It turns red in acids, and substances which turn it red are said to have an *acid reaction*; it turns blue again in alkalis, or in substances having an *alkaline reaction*, and it is unaffected by water and many other substances which have a *neutral reaction*.

*Blue litmus paper* is prepared by dipping unglazed paper in a solution of litmus (prepared by boiling commercial litmus with water and filtering) and drying it. *Red litmus paper* is prepared in a similar way after first adding just sufficient acid to the litmus solution to turn it red.

tube, cut off as shown above the surface of the water. A piece of rubber tube is slipped over it sufficiently long to deliver the gas into the jar. The iron tube is supported by a clamp and heated by a flat-flame Bunsen burner.

Heat the iron tube as strongly as possible, and boil the water in the flask, which should rest on a sand bath. Steam passes over the red-hot nails, and a gas can be collected in the jar.\* When sufficient gas has been collected, first remove the rubber portion of the delivery tube, then the Bunsen with spreading flame, and lastly, when the iron tube is no longer red-hot, the Bunsen underneath the flask.

*Note.*—The water in the flask must be kept boiling while the gas is being collected, or water may be forced back into the iron tube and cause a slight explosion. If it should cease to boil, at once remove the rubber portion of the delivery tube.

Test the gas in the jar with a lighted match. It burns with a practically non-luminous flame. It is *hydrogen*. Turn out the residue in the tube and examine it. The turnings or nails now resemble in appearance the blue-black substance produced when we burnt iron in oxygen (Exp 27). They are, in fact, coated with the same substance—oxide of iron, and this compound is also formed when iron is heated strongly in air (the so-called ‘smithy scales’ which form on the blacksmith’s anvil also consist of it).

### (c) *Magnesium.*

**Exp 38.**—Put into some water a piece of magnesium ribbon, scraped so that the surface is quite bright. You will find that no gas is evolved and the metal is not tarnished.

**Exp 39**—Now repeat Exp. 37, using a coil of magnesium ribbon in place of iron turnings, and replacing the iron tube by one made of porcelain or hard glass. You will find that the same gas is evolved as in Exp 37. Examine the residue in the tube. It is a white substance resembling that obtained by burning magnesium in air or oxygen, it is, in fact, the same substance—oxide of magnesium.

Magnesium then, like iron, reacts with water at red heat with liberation of hydrogen and formation of oxide of magnesium.

\* Before collecting any gas in the jar you must take care that all the air has been driven out of the apparatus. To test this, collect some of the gas in a test-tube, and bring it mouth downwards to a flame. An explosion shows that air is still mixed with the hydrogen. Wait a short time and test again. When the gas ignites with only a very slight ‘pop,’ you may proceed to fill the jars. *Neglect of this precaution and want of care in keeping flames away from the delivery tube have often caused serious accidents,* because air and hydrogen form an explosive mixture.

(d) *Copper.*

**Exp. 40.**—Repeat Exp. 38, using copper instead of iron. You will find that the copper is not tarnished.

Now repeat Exp. 37, using copper turnings and a porcelain or hard glass tube. No gas will be evolved (after the air has been driven out of the apparatus), and on examining the residue in the tube you will find that the copper has undergone no change.

Copper then is not acted upon by water, either in the cold or at a red heat.

The student might continue the experiments with other metals. He would find, for example, that potassium would behave like sodium, zinc like magnesium, tin like copper, and so on.

**28. Composition of Water.**—We have seen in Exps 37 and 39 that iron and magnesium react with steam with liberation of hydrogen and formation of the same substances which are obtained when these metals are burnt in oxygen, *i.e.* the oxides of iron and magnesium. These results can readily be explained if we assume that *water is a compound of hydrogen and oxygen*, for the changes which have taken place can then be represented thus:—

**Water** (composed of **hydrogen** and **oxygen**) acted on by a **metal** yields **hydrogen** and the **oxide of the metal** (composed of the **metal** and **oxygen**).

If this is the true explanation, then we should be able to obtain water by the combination of hydrogen and oxygen.

Before attempting to do this, we will investigate a more convenient method for the preparation of hydrogen in quantity, and will study its properties more fully.

**29. Preparation of Hydrogen.**—

**Exp. 41.**—Introduce into a 12-oz flask, fitted with safety funnel and delivery tube as shown in Fig 12, 10 gms. of zinc, and add 180 c.c. of dilute sulphuric acid.\* Bubbles of gas will be observed to rise at the zinc, and the gas passing out of the delivery tube may be collected in glass cylinders as shown, *taking the precautions referred to in the footnote on p 35* [Reserve the residue in the flask.]

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\* Made by pouring sulphuric acid ("oil of vitriol") slowly with gentle agitation into eight or ten times its volume of cold water. The acid is said to be "diluted" with water.



**Properties of Hydrogen.**—The properties of the gas may be investigated by carrying out the following experiments—

**Exp 42 (a)**—Take a cylinder of the gas, and, holding it mouth downwards, apply a light. Notice that the hydrogen burns with a pale blue practically non-luminous flame, and that the burning takes place only at the *mouth* of the cylinder, *i e* where it has access to air; also that a lighted taper pushed up into the cylinder whilst the hydrogen is burning will be extinguished.

(b) Hold a cylinder full of the gas mouth downwards for a short time; then apply a light and notice that very little of the gas seems to have escaped.

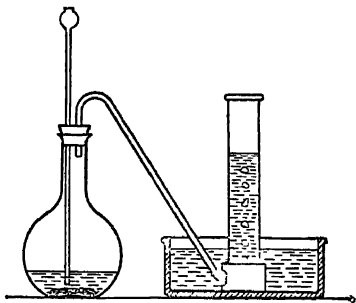


FIG. 12.

(c) Stand a cylinder on the bench mouth upwards, without cover, for a short time. Test this now with a light. You will find no hydrogen there.

(d) Take a *dry* cylinder, somewhat smaller than those used for collecting the gas, and, holding it mouth downwards, transfer the hydrogen from one of the cylinders into it by pouring upwards. The hydrogen will rise in the dry cylinder and displace the air from it. Now apply a light to the mouth of this cylinder and there will be a slight explosion, owing to a small admixture of air during the transference, whilst the gas will burn and moisture appear on the sides of the cylinder.

(e) Invert a cylinder about two-thirds full of hydrogen (the rest being water) in a trough of water. Mark the level of the liquid in the cylinder. After some time examine it again. There is no appreciable change in level, showing that if hydrogen dissolves in water at all its solubility is only very small.

b, c, d of Exp 42 illustrate the extreme lightness of hydrogen.

### 30. Formation of Water by burning Hydrogen in Air.—

**Exp 43**—Take the hydrogen apparatus used above, replacing the long delivery tube by a shorter one leading to one arm of a U-tube containing calcium chloride. Attach a piece of glass tubing, bent as shown in Fig. 13, to the other arm of the U-tube. The object of this tube is to dry the hydrogen before burning it, calcium chloride being a substance which very readily absorbs moisture.\* Place some granulated zinc (about 10 gms) in the flask, and add a little dilute sulphuric acid. A gentle effervescence of hydrogen will take place, and the air will be driven out. Before we light the hydrogen we must be sure that all the air has been expelled from the apparatus by collecting some of the issuing gas in a test-tube placed over the end of the delivery tube, and testing it in the manner already described (see footnote, p. 35).

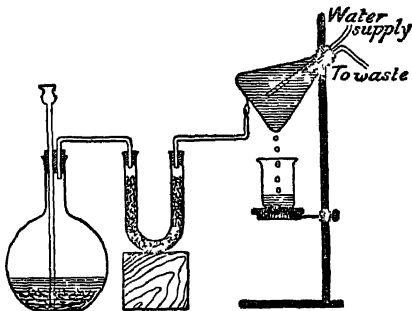


FIG. 13.

While you are waiting for the air to be driven out of the apparatus, fit up a flask with two delivery tubes, one reaching to the bottom of the flask, the other just below the cork, and support it by means of a retort-stand and clamp as shown in the diagram. Connect the delivery tube which reaches to the bottom of the flask to a tap by means of rubber tubing; also attach a piece of rubber tubing to the short delivery tube and allow the loose end of it to dip into a sink. Turn on the tap, water will flow into the flask, fill it, and then overflow into the sink. Leave the tap turned on slightly so that a slow stream of water flows through the flask.

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\* It is obvious that the hydrogen must be *dry*, or the experiment does not prove that the water which collects in the beaker has been produced by the burning of the hydrogen.

When you have lighted the hydrogen jet place the flask in position over it as shown in Fig 13, also place a beaker in the position indicated. Almost immediately moisture appears to be forming on the bottom of the flask, and soon drops of liquid trickle down and fall into the beaker. [The reason for keeping a stream of cold water running through the flask will now be obvious. It keeps the flask cool and aids the condensation of the liquid formed by the burning of the hydrogen.]

What is this liquid? It looks like water. If we examine its properties, we shall find that (1) it is colourless, (2) it has no smell; (3) it has no taste, (4) it does not burn, (5) it leaves no residue on evaporation, (6) it has no action on litmus papers, (7) its density is 1 (1 c c weighs 1 gm), (8) it freezes at  $0^{\circ}\text{C}$ , (9) it boils at  $100^{\circ}\text{C}$ , (10) it restores the blue colour to anhydrous copper sulphate. Hence we conclude that it is *water*.

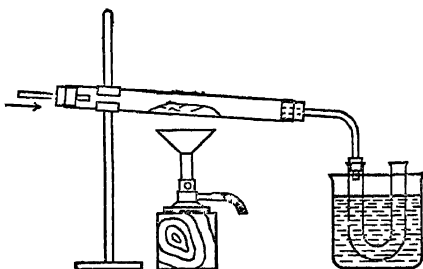


FIG 14.

When hydrogen, then, burns in ordinary air it forms water, it was called *hydrogen* (water-former) on this account. The hydrogen must have combined with either the oxygen or the nitrogen of the air or with both. From our previous experiments (see § 28), we know that it must be with the oxygen *only*. The anticipation made in § 28 that we should be able to obtain water by the combination of hydrogen and oxygen has therefore been realised. The experiment described in the following paragraph shows how this combination may be brought about in a different way.

### Formation of Water by the Action of Hydrogen on Oxides.—

**Exp 44**—Take a piece of infusible glass tubing about 30 cms. long and say 1 cm bore, and put into it a layer of dry copper oxide. Support the tube in a slightly inclined position as shown in Fig 14 and connect the higher end with a supply of dry hydrogen (prepared and dried as in Exp 11). Connect the other end with a U-tube partly immersed in a beaker of water. First the oxide is not heated and there is no apparent change; then it is heated \* strongly, using a flat-flame burner, when it changes gradually into red metallic copper and a liquid collects in the U-tube which can be proved to be water by the usual tests.

The experiment may be repeated using litharge (oxide of lead) or red precipitate (oxide of mercury). In the former case beads of metallic lead collect in the tube and in the latter a mirror of mercury is produced, whilst in both water collects in the U-tube.

We see, then, that when hydrogen is passed over some heated oxides it takes up oxygen, forming water, and leaves behind the metal.

**31. Oxidation and Reduction.**—The *addition of oxygen* to a substance is called *oxidation*. Thus when hydrogen burns in air, when iron rusts or when lead is heated in air, oxygen is taken up and the hydrogen, iron and lead undergo oxidation. On the other hand the *removal of oxygen* from a substance is called *reduction*. The removal of oxygen from heated metallic oxides by hydrogen as in Exp. 44 is an example of reduction, the hydrogen *reducing* the oxide to the metal. But the hydrogen has taken up the oxygen of the oxide and has therefore undergone *oxidation*, i. e. the processes of reduction and oxidation have taken place *simultaneously*, and we may look upon changes such as these from two points of view: (1) as the reduction of the metallic oxide by hydrogen, and (2) as the oxidation of the hydrogen by the metallic oxide. If you refer back to Exp. 12 you will see that charcoal also is able to effect reduction or removal of oxygen, and you will understand the use of coal or coke

The same precautions are necessary here as when the hydrogen was caused to burn as a jet; that is, the issuing gas must be tested to see if it is free from air before the tube is heated. The apparatus, too, should be made *air-tight*. This latter precaution is *very important*.

in the smelting of iron, copper, or other metals from their ores. Hydrogen and carbon are spoken of as *reducing agents*.

**32. Decomposition of Water by the Electric Current—Composition of Water by Volume**—Let us now investigate an entirely different method of determining the constituents of water.

It will be instructive to examine first a peculiar phenomenon which appears when metals are placed in dilute acid.

**Exp. 45—To produce an Electric Current**—For this purpose you will require thin clean plates of copper and zinc,\* say about 15 cm long and 10 cm wide. Dip these separately for a moment into a beaker containing dilute sulphuric acid, and note that the copper plate is unaffected, but the bubbles of gas rise from the zinc plate. Now withdraw the zinc plate, and dipping it in still weaker acid, rub the surface with a little mercury until it shows a bright lustre. The upper part of the plate which stood above the level of the acid in the beaker need not be covered with mercury. Now again dip both the plates in the beaker containing acid; nothing happens at either plate. Bring the upper edges of the two plates together; bubbles of gas rise from the *copper* plate. Separate the plates and bring them together again several times, the action ceases on separation but commences again immediately the plates touch.

Now connect copper wires by binding screws to the upper edges of the two plates.

Observe (1) that when you keep the wires apart there is no evidence of action going on in the beaker, but that when you bring the ends of the wires together the action is set up just as it was when the edges of the plates were brought together, and that now a small spark appears when the wires touch. (2) That if you bring a small compass-needle just below the wire, and then bring the ends into contact, the needle will be turned aside each time you make contact.

If you try to do either of these things simply with two pieces of copper wire, you will then be convinced that there is something present in the wires owing to their attachment to the metal plates in the acid. Metal plates so arranged are called a *voltaiic cell*. By fitting up several of them, and joining the zinc in one cell to the copper in the next by copper wire, and finally attaching two lengths of copper wire, one to the copper in the first cell, and the other to the zinc in the last cell, you may fit up a *voltaiic battery*, and produce stronger effects than you can do with one cell.

\* Plates of other metals may be also tried in the same way.

There is a *third* effect that may be shown to accompany the passage of the electric current along the wires.

**Exp 46** —Procure two pieces of platinum foil about 5 cms long and 2 cms broad. Pick a row of holes down the middle of each and thread the terminal ends of the wires through them. Take now a small beaker of distilled water and dip into it the two platinum plates (they are called *electrodes*), nothing happens. Add a few drops of dilute sulphuric acid to the water; bubbles of gas rise freely from both electrodes.

The current of electricity is unable to pass through pure water and make itself felt, but it can pass through acidulated water. By a suitable arrangement the gases evolved may be collected and examined.

**Exp 47** —Take a large bell-jar and paste a thin strip of paper round the side of it about half-way up, arranging so that the two ends meet and form a circle round the jar. With a sharp file scratch a line just above the strip of paper (which enables you to keep the line straight). When the scratch forms a complete circle take a glass rod, heat the end red-hot in a Bunsen flame, and touch the scratch with it.

The jar will break into two halves. Take the upper half and rub the rough edge with coarse emery paper till it is smooth.

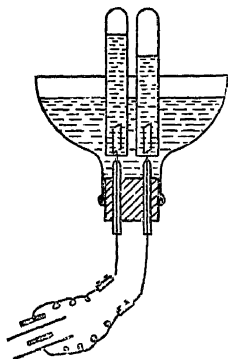


FIG. 15.

Now take two pieces of platinum wire about 6 inches long and attach them to two pieces of platinum foil of the size mentioned in Exp. 46 (in the way described there). Fuse the wires into pieces of narrow glass tubing about 3 inches long, as shown in Fig. 15. Procure a two-holed rubber cork which fits the jar, push the glass tubes into it, and insert the cork (see diagram).

Now pour water, to which a little dilute sulphuric acid has been added, into the jar till the electrodes are covered, also fill two test-tubes with the same liquid and invert them over the electrodes. Connect the wires by binding screws with the leads from a battery of 3 or 4 Grove's cells. As soon as the connection is made gas is seen

to rise from the electrodes and collect in the tubes. Further, the volume of gas collecting over the electrode connected with the zinc plate of the battery (called the *negative pole*) will be found to be twice that collecting over the electrode connected with the platinum plate.

(which corresponds to the copper plate of our simple cell and is called the *positive pole*). Examine the gases with a lighted splint of wood; you will find that the gas collected in larger quantity is *hydrogen*, that in smaller quantity *oxygen*.

Subject to the possibility that it is something in the sulphuric acid with which we are at present insufficiently acquainted that gives us the hydrogen and oxygen, we should conclude that water yields by its decomposition hydrogen and oxygen, and further that it is composed of these two elements *in the proportion of two to one by volume*. That this is the case may be conclusively proved by the following experiment \*—

**Exp. 48**—A long graduated glass tube (called a *eudiometer*), having two platinum wires passed into it near one end, which is closed (Fig. 16), is taken and filled with mercury and inverted in mercury. Some hydrogen is passed in, and then exactly half the volume of oxygen.† On connecting the platinum wires with a battery and induction coil and passing an electric spark through the mixture there is an explosion. After a time we find the mercury fills the entire tube. This proves that the gases have completely combined and that they were present in the proper proportions to form water. Cavendish was the first to establish this fact (1781).

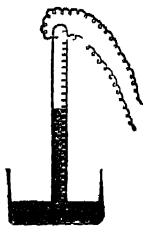


FIG. 16.

We have now determined the quantitative composition of water in two ways. in Exp 47 by *decomposing* it into its constituent elements, *i. e* by *analysis*, in Exp 48 by *combining* the constituent elements, *i. e* by *synthesis*.

\* The student is not advised to perform this experiment.

† The most convenient way is to use the mixture of hydrogen and oxygen produced by the electrolysis of water. The gases are then present in the correct proportion.

## QUESTIONS — CHAPTER IV.

1. What happens when dilute sulphuric acid is poured upon zinc? How would you collect the gas given off? Sketch the apparatus you would use. Describe experiments to show that it is a very light substance.
2. How would you prove conclusively that when hydrogen burns in air water is formed?
3. Describe all that you may see when a piece of sodium is thrown on water in a dish. How does the water differ, after the sodium has disappeared, from pure water?
4. What metals are known to you capable of decomposing water? How do they act respectively? Sketch the apparatus that would be required to collect the hydrogen evolved by the use of any one of these metals.
5. How has the composition of water by volume been established analytically and synthetically?
6. Describe how you would proceed to prepare water from a metallic oxide by the action of hydrogen. Sketch the necessary apparatus.
7. What do you understand by the terms *oxidation* and *reduction*. Give examples of these processes.



## CHAPTER V.

### ACIDS, SALTS, BASES.

#### 33. Properties of Acids.—

##### (a) Sourness.

**Exp 49 (a)** —Introduce *one drop* of dilute \* hydrochloric acid (*spirit of salt*) and one drop of dilute sulphuric acid respectively into clean test-tubes and nearly fill the tubes with water. Shake up and then taste the liquids. They are sour.

Vinegar also is sour. *Sourness* is a characteristic property of a large class of bodies called *acids*.

##### (b) Action on Litmus.

**Exp 49 (b)** —Pour a little dilute hydrochloric acid and a little dilute sulphuric acid into separate beakers and dip pieces of blue litmus paper into them. The colour changes to *bright red*.

##### (c) Action on Metals.

**Exp 49 (c)** —Fill a test-tube about one-third full of dilute sulphuric acid and introduce some small pieces of magnesium ribbon. Notice that there is a violent effervescence of gas and that the tube soon becomes warm. After a short time apply a light to the mouth of the tube. The gas ignites with a slight explosion and burns with an almost non-luminous flame. It is *hydrogen*.

You may find that when most of the magnesium has dissolved colourless crystals separate out in the tube. If they do not, filter the liquid, evaporate to small bulk in a porcelain dish, and allow to cool. Colourless crystals separate out. These consist of a substance called *magnesium sulphate*. Magnesium has taken the place of the hydrogen of the acid. Instead of *sulphuric acid* and *magnesium*, we have now *hydrogen* and *magnesium sulphate*.

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\* "Dilute" hydrochloric acid is obtained by adding two or three volumes of water to one volume of the strong acid.

**Exp 49 (d).**—We have already found in Exp 41 that hydrogen is evolved by the action of dilute sulphuric acid on the metal zinc. Examine the residue in the flask (which you have reserved). You will observe that colourless crystals have separated out. These consist of *white vitriol* or *zinc sulphate*. The zinc has replaced the hydrogen of the acid, with formation of zinc sulphate.

In order to obtain the zinc sulphate free from metallic particles, pour a little water into the flask and warm till the crystals dissolve. Now filter, evaporate the filtrate slightly, and cool. Crystals separate out.

Similar results are obtained if iron is treated with dilute sulphuric acid; also if hydrochloric acid or acetic acid is used with any of these metals instead of sulphuric acid. Here, then, we have a third characteristic of an acid, namely, that it acts upon certain metals, such as iron, zinc, and magnesium, with liberation of hydrogen and formation of crystalline substances.

**34. Salts.**—The crystalline substances produced by the action of metals on acids are termed *salts*. Let us see whether or not they behave like acids towards litmus.

**Exp 50**—Filter off the crystals of magnesium sulphate obtained in Exp 49 (c). Wash them carefully\* with a little water, and then dissolve in water. Test the solution with (1) blue litmus paper, (2) red litmus paper. You will find that neither is affected, i. e. magnesium sulphate is *neutral* to litmus.

Repeat the experiment with the crystals of white vitriol obtained in Exp. 49 (d). You will find that white vitriol is also neutral to litmus.

The replacement of hydrogen in sulphuric acid by magnesium or zinc has removed from the acid one of its characteristic properties—that of turning blue litmus red. The salts derived from other acids are also neutral to litmus in the majority of cases. Since, then, an acid is no longer an acid after its hydrogen has been removed, it follows that *hydrogen is an essential constituent of acids*.

The salts derived from sulphuric acid are called *sulphates*, those from hydrochloric acid *chlorides*; those from nitric acid *nitrates*, and so on.

\* The success of this experiment depends upon the care with which the crystals are washed. Unless the adhering acid is completely removed, the solution of the salt will of course be acid to litmus.

### 35. Formation of Acids from Non-metals.—

**Exp 51.**—Burn some sulphur in air as in Exp 24. Remove the deflagrating spoon, pour a little water into the jar, drop in a piece of blue litmus paper and at once cover with a greased glass plate. Shake up. Notice that the white fumes disappear and the blue litmus is reddened, showing that an acid has been formed. Invert the jar in a trough of water and remove the glass plate, the water rises in the jar.

Pour a little of the acid liquid in the jar into a porcelain basin and boil it. Notice that after a time the smell disappears. Now test the remaining liquid with blue litmus paper; the litmus is not affected.

The results obtained in the previous experiment are in accordance with the following explanation:—The sulphur in burning combines with oxygen to form an oxide of sulphur—*sulphur dioxide*. This substance is a gas which dissolves very readily in water, with which it combines forming an acid—sulphurous acid. [That sulphur dioxide *alone* is not an acid is proved by the fact that when quite dry it does not affect dry litmus paper; it is only when the gas is dissolved in water that it acquires acid properties therefore in all probability the solution contains a compound of sulphur dioxide and water, though such a compound has never been isolated.] The water rises in the jar to take the place of the oxygen which has been removed.

The effect of boiling the acid solution is to decompose the acid present and drive off the sulphur dioxide in the form of gas.

You might similarly repeat Exp 19, and show by means of litmus solution that the water in the trough becomes acid. Here the white powder formed by the combination of phosphorus with the oxygen of the air (phosphorus pentoxide) dissolves in the water, and unites with it to form an acid—phosphoric acid. This is a general property of non-metals, *i. e.* they combine with oxygen to form oxides, which unite with water with formation of acids. Such oxides are called *acidic oxides*.

**36. Alkalies: Caustic Soda, Sodium Hydroxide.**—We have already learnt (Exp 36) to recognise this class of substances by the use of litmus solution. They possess the

property of restoring the colour to litmus which has been reddened by the addition of acid. But they have another important property which we shall now examine.

One of the most important substances belonging to this class of bodies is that known as *caustic soda*.

Caustic soda is a substance of considerable interest and importance, and is manufactured in large quantities for various purposes, but especially for soap-making. We met with it when describing the behaviour of sodium towards water.

**Exp 52** —Examine a piece of caustic soda and observe that—

- (a) It is a white solid, but does not seem to be crystalline
- (b) If left exposed to the air, it becomes moist, that is, it *deliquesces*. It would, if left long enough, run down to a liquid. It absorbs moisture from the air. Such bodies are termed *hygroscopic* or *deliquescent*.
- (c) It dissolves very readily, as do most deliquescent bodies, in water, and considerable heat is developed during solution. The liquid thus formed has a soapy feeling.
- (d) This solution turns reddened litmus blue

Carefully add to this blue solution a solution of hydrochloric acid until the colour *just* becomes red. (The hydrochloric acid is conveniently run in from a long tube with a stop-cock at the bottom called a *burette*.) We have now, as it were, balanced the alkali with acid. The slightest quantity of caustic soda solution will change the colour to blue again. We have here practically a *neutral* solution. *How does it differ from the acid and the alkali?*

Boil it down to dryness. Notice that the solid produced is not like caustic soda. Taste it. You will recognise it as *common salt*.

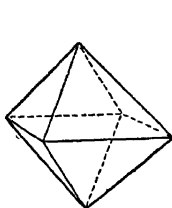
The salt has been produced by the replacement of the hydrogen of the acid by the metal sodium, *i. e.* it is the sodium salt of hydrochloric acid, or *sodium chloride*. Here, then, we have a second method of preparing salts, namely, by the action of an alkali on an acid.

*An alkali is a substance which possesses the property of restoring the blue colour to reddened litmus, and of neutralising acids with formation of salts.*

**Caustic Potash, Potassium Hydroxide**, may be examined in the same way as was caustic soda. It is an exactly similar body, and could not be distinguished from it by ordinary means. It, too, will neutralise acids, and when

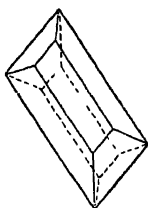
Alum crystallises with  $24 \text{ H}_2\text{O}$ ;  $10 \text{ H}_2\text{O}$  separate at  $100^\circ \text{C}$ , a further  $9 \text{ H}_2\text{O}$  at  $120^\circ \text{C}$ , and nearly the whole of the remainder at  $280^\circ \text{C}$ . In some cases, indeed, such as crystallised sodium carbonate or washing soda,  $\text{Na}_2\text{CO}_3 + 10 \text{ H}_2\text{O}$ , the salt loses water or *effloresces* at ordinary temperatures in a dry atmosphere.

The amount of water of crystallisation which attaches itself to a salt varies according to the temperature at which the crystals form. Thus, from a solution of sodium sulphate, crystals of  $\text{Na}_2\text{SO}_4 + 7 \text{ H}_2\text{O}$  can be obtained at temperatures below  $26^\circ$ , or crystals of  $\text{Na}_2\text{SO}_4 + 10 \text{ H}_2\text{O}$



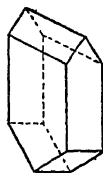
Alum  
 $\text{K}_2\text{SO}_4 \text{ Al}_2(\text{SO}_4)_3 \cdot 24 \text{ H}_2\text{O}$ .

FIG. 33.



Washing soda.  
 $\text{Na}_2\text{CO}_3 \cdot 10 \text{ H}_2\text{O}$ .

FIG. 34.



Epsom salts.  
 $\text{MgSO}_4 \cdot 7 \text{ H}_2\text{O}$ .

FIG. 35.

(Glauber's salt) at temperatures below  $34^\circ$ ; while above  $34^\circ$  crystals of  $\text{Na}_2\text{SO}_4$  are obtained. Epsom salts,  $\text{MgSO}_4 + 7 \text{ H}_2\text{O}$ , furnishes another example, giving  $\text{MgSO}_4 + 6 \text{ H}_2\text{O}$ . Frequently, salts which at ordinary temperatures separate from solution in the anhydrous condition, possess water of crystallisation when crystallised at low temperatures. Thus if a concentrated solution of common salt be allowed to stand at ordinary temperatures crystals of  $\text{NaCl}$  are obtained, but at  $-10^\circ \text{C}$ . crystals of  $\text{NaCl} + 2 \text{ H}_2\text{O}$ .

As examples of the crystalline forms assumed by salts containing water of crystallisation, we may consider three very common substances, viz. alum, washing soda, and Epsom salts. Figs. 33, 34 and 35 represent crystals of these substances, and it will be noticed how widely the three crystals differ in shape.

117. **Compounds of Water with Oxides** — We have seen in discussing acids and bases that many oxides combine directly with water. The products vary in stability, but are as a whole very much more stable than those obtained when salts and water combine.

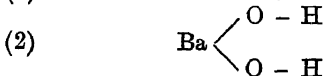
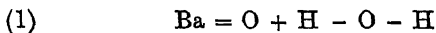
In many cases great heat is evolved when oxides and water unite, thus demonstrating the vigorous nature of the action.

**Exp 98.**—Pour a *little* water on to some quicklime contained in a porcelain dish. Note the clouds of steam formed, showing that much heat is evolved during the combination. Dip a thermometer in the mixture and note the rise of temperature.

Other examples of oxides which evolve much heat on combination with water are  $\text{BaO}$ ,  $\text{SO}_3$ ,  $\text{P}_2\text{O}_5$ . To bring about the decomposition of the compounds produced a correspondingly large amount of heat must be supplied, *i. e.* a high temperature is necessary.

To explain the greater stability of the compounds of water with oxides as compared with the compounds with salts, it is supposed that in the latter the water is present in *whole molecules* loosely combined with the molecule of the salt, whereas in the former it has completely lost its identity. Thus crystallised copper sulphate may be formulated  $\text{CuSO}_4 + 5 \text{H}_2\text{O}$  or  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , but barium hydroxide must not be represented  $\text{BaO} + \text{H}_2\text{O}$  or  $\text{BaO} \cdot \text{H}_2\text{O}$ , *i. e.* as containing a molecule of  $\text{BaO}$  and a molecule of water; it must be written  $\text{Ba}(\text{OH})_2$ , *i. e.* it contains two *hydroxyl* ( $\text{OH}$ ) groups united to an atom of barium.

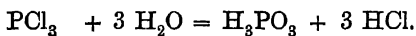
The constitutional formulæ, adopting the two methods, will bring out the difference clearly



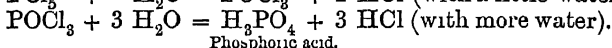
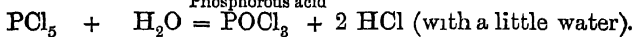
It is supposed that all the compounds of water with oxides contain one or more ( $\text{OH}$ ) groups, and they are consequently called *hydroxides*, whereas the combinations of salts and water are termed *hydrates*.

**Action of Metals on Water**—This has been fully discussed in § 27, and does not require further treatment here.

**118. Action of Water on Compounds containing Chlorine.**—Many compounds of non-metals with chlorine or chlorine and oxygen react vigorously with water producing hydrochloric acid and another acid (or sometimes an oxychloride). Such substances are phosphorus trichloride,  $\text{PCl}_3$ , phosphorus pentachloride,  $\text{PCl}_5$ , phosphorus oxychloride,  $\text{POCl}_3$ , and sulphuryl dichloride,  $\text{SO}_2\text{Cl}_2$ . The phosphorus compounds react with water according to the following equations.—

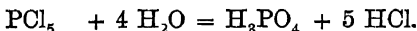


Phosphorous acid

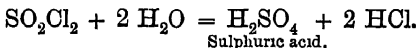


Phosphoric acid.

On combining the last two equations to represent the reaction of  $\text{PCl}_5$  with excess of water we get—



The reaction between sulphuryl dichloride and water is represented thus—



Sulphuric acid.

**119. Tests for Water.**—To distinguish water from other colourless liquids the following tests may be applied.—

(1) Add a few drops of the liquid to a small quantity of anhydrous copper sulphate (prepared by igniting some powdered blue vitriol in a crucible till it is perfectly white and allowing it to cool in a desiccator). Water rehydrates it and changes the colour from white to blue.

(2) Add a little of the liquid to some quicklime (see Exp. 98).

(3) Drop a small pellet of sodium or potassium (about the size of a pea) on to a portion of the liquid. If the liquid is

water hydrogen will be evolved and will take fire in the case of potassium.

To decide whether water is *pure* or not its physical properties may be utilised. The liquid should

- (a) be colourless, tasteless and odourless;
- (b) freeze at  $0^{\circ}\text{C}$ . ;
- (c) boil at  $100^{\circ}\text{C}$ . under 760 mm pressure.

Moreover, pure water should give no precipitate or coloration with (1) *silver nitrate* (showing absence of chlorides), (2) *barium chloride* (showing absence of sulphates), (3) *Nessler's solution* (showing absence of ammonia), (4) *lime water* (showing absence of carbonates).

### HYDROGEN PEROXIDE, $\text{H}_2\text{O}_2$ .

120. This substance has been found in very small quantities in rain and snow, and also in the water formed by the combustion of hydrogen.

It is produced in small quantity during the slow oxidation of phosphorus and in larger quantities when turpentine is shaken with water in the presence of air.

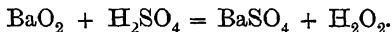
**Preparation.**—The peroxides of the alkali and alkaline earth metals yield hydrogen peroxide on treatment with dilute acids. Either barium peroxide or sodium peroxide is generally used in practice. The following are the details of the preparation of the pure substance using barium peroxide and sulphuric acid :—

Some dilute sulphuric acid is placed in a beaker and surrounded by a freezing mixture of ice and salt to keep its temperature low. A cream of barium peroxide and water which has also been cooled in a freezing mixture is then slowly run into the acid with constant stirring. Barium sulphate is precipitated and hydrogen peroxide goes into solution. Excess of barium peroxide must not be added or it will decompose the hydrogen peroxide. The best way is to add rather less than an equivalent quantity of barium peroxide (*i.e.* keep the solution acid to test paper) and remove the excess of acid by barium carbonate. The barium sulphate and any excess of barium carbonate are filtered off,



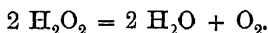
and the filtrate evaporated on the water-bath, the temperature not being allowed to rise above  $75^{\circ}\text{C}$ , or the hydrogen peroxide will be decomposed. By this means a considerable part of the water is driven off. The final purification is accomplished by fractionally distilling the liquid under reduced pressure (about 10 mm. of mercury). Water comes off first, and when this has all been removed the receiver is changed, on continuing the distillation hydrogen peroxide passes over in an almost pure state.

The equation representing the formation of hydrogen peroxide from barium peroxide and sulphuric acid is—



**121. Properties.**—Hydrogen peroxide is a thick liquid with a specific gravity about 1.5, it is colourless in small masses, but in large masses it has a decidedly bluer colour than water.

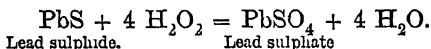
Hydrogen peroxide is remarkable for the ease with which it breaks up into water and oxygen according to the equation—



The pure substance decomposes with explosive violence on slight rise of temperature, and the dilute aqueous solution loses oxygen rapidly on boiling.

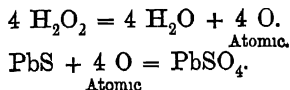
Hydrogen peroxide affords another interesting example of catalysis, for its dilute solution decomposes rapidly at ordinary temperature in contact with certain metals such as finely-divided platinum, the latter undergoing no change.

**122. Oxidising Action of Hydrogen Peroxide.**—Owing to the ease with which hydrogen peroxide parts with an atom of oxygen it is a powerful oxidising agent. Thus it converts lead sulphide into lead sulphate, according to the equation—

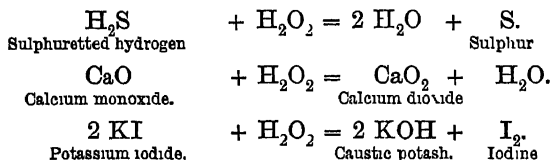


Ordinary molecular oxygen will not bring about this change except on heating. We have, however, seen in

discussing ozone that atomic oxygen is more active than molecular oxygen, and it is the atomic oxygen produced when hydrogen peroxide decomposes which acts so readily on the lead sulphide. We may therefore represent the reaction in two stages—

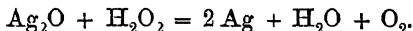


This reaction is made use of in restoring the colour of old pictures which have been blackened by the action of sulphuretted hydrogen on the lead paint. The hydrogen peroxide converts the *black* lead sulphide into *white* lead sulphate. Other examples of its oxidising action are represented in the following equations:—



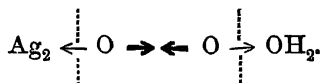
Hydrogen peroxide possesses the power of bleaching many vegetable and animal colours, and is much used for bleaching hair, silk, ivory, etc. It also destroys decaying organic matter, and consequently finds application as a disinfectant. Both these properties depend upon its oxidising action.

**123. Reducing action of Hydrogen Peroxide.**—When silver oxide,  $\text{Ag}_2\text{O}$ , is treated with hydrogen peroxide a mutual decomposition takes place, the silver oxide is reduced to silver and the hydrogen peroxide to water, and a molecule of oxygen is evolved—

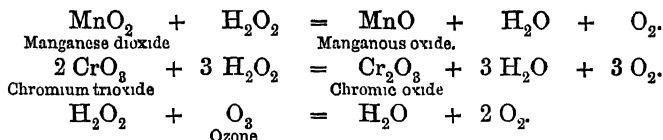


The explanation of this is that both silver oxide and hydrogen peroxide contain a loosely-combined atom of

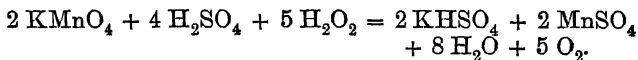
oxygen, and the attraction of these two atoms for one another is greater than their respective attractions for silver and water. They consequently break away and unite to form a molecule of oxygen. We may represent this in the following way, a thick arrow indicating greater attracting force than a thin arrow—



Other examples of the reducing action of hydrogen peroxide explained in a similar manner are represented by the following equations:—



Potassium permanganate in acid solution is also reduced—



**124. Experiments with Hydrogen Peroxide.**—To illustrate the preparation and properties of hydrogen peroxide, the following course of procedure may be adopted:—

**Exp 99** —Add 10 c.c. of concentrated sulphuric acid to 200 c.c. of water, and allow the mixture to stand till it becomes quite cold; now add little by little, with constant stirring, about 30 grammes of barium peroxide. Allow to settle, and decant off the clear liquid. It is a dilute solution of hydrogen peroxide, and the following experiments may be performed with it—

(1) To some of the liquid add potassium iodide, iodine will be liberated, and the solution become brown. The equation for the reaction which takes place has been given in § 122

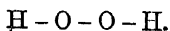
(2) Make a dark stain of sulphide of lead on filter paper by first moistening it with a solution of a lead salt, say the acetate, and then exposing this to sulphuretted hydrogen. Steep the paper in a little of the hydrogen peroxide solution and it will become white, the black sulphide of lead having been transformed into the white sulphate, as shown in the equation given above.

(3) Add silver nitrate to some of the solution, and then caustic soda; a black precipitate of hydrated oxide of silver will be formed, and this in contact with the hydrogen peroxide will undergo decomposition in the manner already described; the effervescence of gas which is seen to occur may be shown to be due to oxygen.

### 125 Proof of the Composition of Hydrogen Peroxide.—

The following method may be adopted to prove that the ratio of oxygen to hydrogen in hydrogen peroxide is twice as great as it is in water:—A given weight (about 0.2 gramme) of the pure substance, prepared as already described, is introduced into a flask, which is then filled up completely with recently-boiled water. This flask is provided with a delivery tube which does not reach below the bottom of the cork, and is also filled with water. The flask is heated at first to about  $80^{\circ}$  C., but finally (when the evolution of gas slackens) to the boiling-point. Oxygen is evolved, and is collected over water in a measuring tube of about 100 c.c. capacity. The weight of oxygen evolved can be calculated from its volume, and if the hydrogen peroxide is pure it will be found that 34 parts by weight of it yield 16 parts by weight of oxygen. The remaining  $34 - 16 = 18$  parts by weight consist of water. Now 18 parts by weight of water contain 16 parts by weight of oxygen and 2 parts by weight of hydrogen. Therefore the ratio of oxygen to hydrogen in hydrogen peroxide is  $2 \times 16 : 2 = 16 : 1$ , which is twice as great as the ratio in water (approximately 8.1).

The simplest formula for hydrogen peroxide would be HO, for 1 and 16 are the atomic weights of hydrogen and oxygen. It has been proved, however, by a physical method of determining molecular weights (the lowering of freezing-point method), that the molecular weight is not 17 as it would be if the formula were HO, but 34, which corresponds to the formula  $H_2O_2$ . The doubled formula possesses the advantage that it fits in with the usual valencies of hydrogen (one) and oxygen (two). Thus the structural formula would be—



If however the single formula were adopted, both oxygen and hydrogen must have the same valency, the structural formula being  $\text{H} - \text{O}$ .

### QUESTIONS.—CHAPTER XIII.

1. Describe carefully a synthetic method of determining the composition of water by volume.
2. How may the volumetric composition of water be determined analytically?
- 3 In a determination of the volumetric composition of water by Bunsen's method the following readings were taken—

Distance of closed end of tube from mercury in trough (Neglect any slight changes)	72 c.m.
Height of column of mercury above mercury in trough after introduction of oxygen	54 c.m.
Height of column of mercury above mercury in trough after introduction of hydrogen	14 c.m.
Height of column of mercury above mercury in trough after explosion and cooling to atmospheric temperature	23.85 c.m.
Temperature of the air throughout the experiment	16° C.
Atmospheric pressure throughout the experiment	75 c.m.
Pressure of aqueous vapour at 16° C.	1.35 c.m.

Calculate the volume of hydrogen combined with 1 volume of oxygen.

4. How would you prove by experiment that steam contains its own volume of hydrogen?
5. Describe the method by which Dumas and Stas determined the composition of water by weight.
6. Pure hydrogen is passed over heated oxide of copper, and the water which forms is collected; if the loss in weight of the oxide of copper be 4.20 grammes, and

- the weight of the water obtained 4.73 grammes, determine the amount of hydrogen and oxygen in 100 grammes of water
7. Trace the changes in volume that occur when heat is applied to a mass of ice until it melts and passes into vapour.
  8. Define the *unit quantity of heat*. What name is given to this unit?
  9. What is meant by "specific heat"? The specific heat of air is 0.24, find how much the temperature of a cubic metre of air will be raised by the heat given off during the cooling of 100 grammes of water from  $25^{\circ}\text{C}$  to  $20^{\circ}\text{C}$ .
  10. A kilogramme of water at  $0^{\circ}\text{C}$  is intimately mixed with a kilogramme of mercury at  $100^{\circ}\text{C}$ , until both acquire the same temperature, the specific heat of mercury being 0.033, find the increase in temperature of the water.
  11. What do you understand by the term "latent heat"? Under what circumstances does heat become latent, and what becomes of the heat thus rendered latent?
  12. How much ice at  $0^{\circ}\text{C}$ . will a kilogramme of mercury at  $100^{\circ}\text{C}$ . just suffice to melt?
  13. How many units of heat are required to raise the temperature
 

(a) of 100 grammes of water  $10^{\circ}\text{C}^{\circ}$  ;

(b) " " " " , mercury  $10^{\circ}\text{C}^{\circ}$  ;

 and to convert 100 grammes of water at  $0^{\circ}\text{C}$ . into steam at  $100^{\circ}\text{C}^{\circ}$ . ?
  14. Describe an experiment showing that water vapour exerts a pressure at ordinary temperature.
  15. Explain what is meant by the *boiling-point of a liquid*.
  16. When is a solution said to be *saturated*? What amount of potassium nitrate (see table, § 115) would be required to form a saturated solution in 150 c.c. of water, (a) at zero, (b) at  $50^{\circ}\text{C}$ . ?

- 17 State Henry's Law. What volume of  $\text{CO}_2$  will dissolve in 250 c.c. of water under standard pressure, (a) at zero, (b) at  $20^\circ \text{C}$ , and what at these temperatures when the pressure is that of 76 mm. of mercury, and when it is three atmospheres?
18. A mixture of carbon dioxide and oxygen containing 95 per cent by volume of the latter gas is shaken up with 500 c.c. of water at standard temperature and pressure; what volume of each gas will be dissolved?
- 19 In what respects does a typical sample of rain water differ from the water of the Thames?
- 20 How does it come about that sea water contains more matter in solution than river water?
21. What are the essential qualities of good drinking water?
22. Why is more soap required to produce a permanent lather with *hard* water than with *soft* water?
23. State the constituents to which the temporary and permanent hardness of water are respectively due.
24. Explain the circumstances under which the addition of lime-water renders a water soft, and state why it does so.
25. How can calcium carbonate be made to dissolve freely in water, and how may the calcium carbonate be precipitated out of such water again without the addition of chemical reagents?
26. How can permanent hardness be removed from water?
- 27 How can the temporary and permanent hardness in a sample of water be determined?
28. What is meant by *water of crystallisation*? Give examples.
29. Distinguish between a *hydrate* and a *hydroxide*, and give examples of each.
- 30 Write down in separate paragraphs (a) the physical, (b) the chemical properties of water.
31. Make a list of those properties of water which you regard as being absolutely characteristic of that body.
32. How would you test whether a given colourless liquid is water or not?

33. Describe how you would test the purity of a sample of water
34. How is hydrogen peroxide prepared? What is its action on (1) potassium iodide, (2) lead sulphide, (3) silver oxide?
35. It has been said that hydrogen peroxide behaves both as an oxidising and a reducing agent; explain this statement, and illustrate your remarks by references to reactions.
36. How can the composition of hydrogen peroxide be proved?



## CHAPTER XIV.

### THE HALOGENS.

126 A COMPARISON of the physical and chemical properties of the four elements, fluorine, chlorine, bromine and iodine, and of their compounds, readily leads one to regard these elements as forming a natural group.

This is shown in two ways, firstly by the *resemblance* in properties, and secondly by the *gradual transition* in their properties, which proceeds always in the same order, viz. in the order of their atomic weights. A general survey of the group will illustrate this.

**Physical Properties of these Elements.**—Fluorine is a gas which condenses to a liquid when cooled to a temperature of  $-187^{\circ}\text{C}$ . ; it possesses a very faint greenish-yellow colour ; chlorine is a much more readily-condensable gas, and has a distinct greenish colour, bromine is a dark red liquid boiling at  $59^{\circ}\text{C}$ . and solidifying at  $-7^{\circ}\text{C}$  ; whilst iodine is a black crystalline solid which boils at  $184^{\circ}\text{C}$ ., its vapour being of a beautiful violet colour.

In the gaseous condition these elements have a very irritant action on the mucous membrane, which is, however, much less marked in the case of iodine than in that of the other three elements. The halogens have an odour resembling that of seaweed if they are in a largely-diluted condition.

Their solubility in water follows the order of their atomic weight ; chlorine, the most soluble (fluorine decomposes water), dissolving in about half its volume of water, brom-

ine to the extent of three parts in 100 of water, whilst iodine is only very slightly soluble in water, but dissolves readily in alcohol, ether, bisulphide of carbon, or in a solution of potassium iodide.

When chlorine is passed into water to saturation at  $0^{\circ}\text{C}$ ., yellow crystals having the composition  $\text{Cl}_2 \cdot 8 \text{H}_2\text{O}^{(?)}$  separate out. On warming these crystals they readily decompose with the evolution of chlorine. Bromine under similar circumstances forms crystals having the composition  $\text{Br}_2 \cdot 10 \text{H}_2\text{O}^{(?)}$ .

**127 General Chemical Properties.**—All the halogens combine directly with hydrogen to form gases (except hydrofluoric acid, which is a liquid boiling at  $19.5^{\circ}\text{C}$ .) These hydrides of the halogens are very soluble in water, giving rise to strongly acid solutions. The readiness with which combination with hydrogen takes place *decreases* as the atomic weight *increases*. Thus, fluorine and hydrogen combine even in the dark and at very low temperatures, whereas chlorine requires the influence of heat or of chemically active light rays, and bromine and iodine are induced to combine with hydrogen with much greater difficulty.

Moreover, the stability of the products,  $\text{HF}$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ , shows a falling off in the order named.

The hydrogen atom of each of these compounds can be replaced by the metals potassium and sodium to form a group of bodies,  $\text{KF}$ ,  $\text{NaF}$ ,  $\text{KCl}$ , etc., all of which closely resemble *sea-salt*. It is from this that the name *halogens* is derived ( $\alpha\lambda\varsigma$ , sea-salt, and  $\gamma\epsilon\nu\nu\acute{\alpha}\omega$ , I produce).

The tendency of the halogens to combine with oxygen *increases* as the atomic weight *increases*. Thus, whilst fluorine forms no oxide, and chlorine can only be made to combine with oxygen indirectly giving rise to unstable oxides, iodine is directly oxidised by nitric acid, and its oxide is much more stable. Bromine occupies an anomalous position here, as no oxide of it is known.

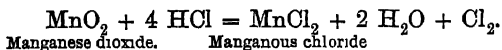
The interaction of the halogens and water affords another example of this gradation in properties as we pass from

fluorine to iodine. Fluorine decomposes water immediately at ordinary temperatures, a vigorous reaction taking place; much of the oxygen liberated is in the form of ozone. Chlorine and bromine act on water at ordinary temperatures only in the presence of sunlight, and no ozone is formed; chlorine is much the more active of the two. Iodine does not decompose water.

### CHLORINE, $\text{Cl}_2$ .

**128. Occurrence.**—Chlorine occurs very abundantly in nature, but never in the free state. Its most important compound is common salt (sodium chloride), which forms large deposits in various parts of the world, *e. g.* Cheshire in England, and Wieliczka in Galicia. Common salt is also the chief solid constituent of sea water. The enormous salt deposits at Stassfurt in Germany are composed largely of the chlorides of potassium and magnesium. Free hydrochloric acid is a constituent of the gastric juice.

**129. Preparation.**—Chlorine is usually prepared in the laboratory by heating manganese dioxide with concentrated hydrochloric acid. The reaction which takes place is represented by the equation—



**Exp. 100.**—Introduce about 100 grammes of manganese dioxide, in small lumps, into a large flask, and just cover it with strong hydrochloric acid. Close the mouth of the flask with an india-rubber cork carrying a safety funnel and delivery tube. Support the flask on a sand-bath by means of a retort-stand, and connect it with a wash-bottle containing a little water. Provide the wash-bottle with a delivery tube reaching to the bottom of a glass cylinder as shown in Fig. 36. Now apply a gentle heat to the flask, when chlorine is evolved mixed with hydrochloric acid. For a short time, both the chlorine and the hydrochloric are absorbed by the water in the wash-bottle. Soon, however, the solution becomes saturated with chlorine which then passes on, whilst the hydrochloric acid, being very much more soluble, continues to be absorbed in the wash-bottle. The chlorine

is collected in glass cylinders by displacement of air, it cannot be collected over water or mercury because it is soluble in the former and attacks the latter, it may, however, be collected over strong brine in which it is only slightly soluble.

If the gas is required *dry* it may be passed through one or more wash-bottles containing concentrated sulphuric acid before being collected as above.

Instead of using hydrochloric acid in the preparation of chlorine just described, a mixture of common salt and

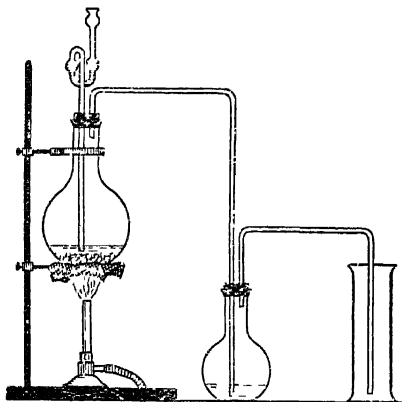
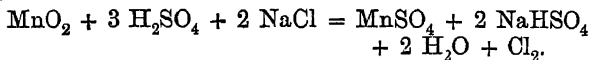
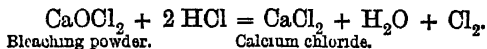


FIG 36

strong sulphuric acid may be employed. The equation representing the reaction which takes place then becomes—



The most convenient method of preparing chlorine is to act on bleaching powder with dilute hydrochloric acid. The bleaching powder is used in the form of small lumps, obtained by first pressing it into a cake and then breaking this cake up. Under these conditions chlorine is evolved at a convenient rate without the application of heat—



**130. Properties**—Chlorine is a greenish-yellow gas which has a very irritating action on the mucous membrane. It is soluble in water, one volume of which takes up about two volumes of the gas at ordinary temperatures. Chlorine is a heavy gas, its density being about two and a half times that of air. Its molecule contains two atoms, except at very high temperatures, when partial dissociation into single atoms takes place, as shown by the fall in vapour density.

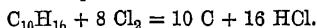
Chlorine is a very active substance. It combines directly with many elements and compounds at the ordinary temperature, very frequently with incandescence.

**131. Combination of Chlorine and Hydrogen.**—When chlorine and hydrogen are mixed and exposed to direct sunlight they combine with explosion, hydrochloric acid being formed. Burning magnesium wire, which gives out light very rich in chemically active rays, also causes the mixture to explode. In diffused daylight combination takes place gradually, and in the dark hydrogen and chlorine do not unite. By proceeding as described in the following experiment it is possible to burn hydrogen quietly in chlorine.

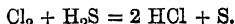
**Exp 101**—Prepare a jar of chlorine from manganese dioxide and hydrochloric acid as described above, and introduce a lighted jet of hydrogen into it. It continues to burn with the production of fumes of hydrochloric acid, which may be made more visible by bringing a drop of ammonia liquor to the mouth of the jar.

The affinity of chlorine for hydrogen is so great that it is able to extract it from many compounds, such as turpentine ( $C_{10}H_{16}$ ), sulphuretted hydrogen ( $H_2S$ ) and water.

**Exp 102.**—Introduce a piece of blotting-paper soaked in turpentine into a jar of chlorine. The turpentine takes fire, white fumes of hydrochloric acid are formed and a black deposit of free carbon settles on the sides of the jar.



**Exp 103**—Pass chlorine for some minutes through about 50 c.c. of water, and to about 20 c.c. of this add a solution of sulphuretted hydrogen, hydrochloric acid is formed, the liquid becoming turbid owing to the separation of sulphur, according to the equation—



**Exp. 104.**—Fill a Cowper's tube with chlorine water (see

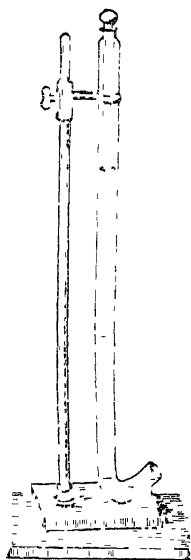
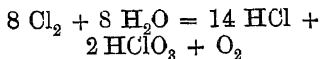


FIG. 37.

Fig 37) and expose to direct sunlight, bubbles of gas will be seen to rise in the liquid. When sufficient gas has collected it may be tested with a glowing splinter, and will be found to be oxygen. The change which has taken place is represented by the equation—



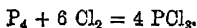
Chlorine will, moreover, support the combustion of a candle or of coal gas, on account of its affinity for hydrogen. The substances of which candles are composed consist either entirely, or at any rate largely, of carbon and hydrogen, and when a lighted candle is lowered into a jar of chlorine it continues to burn with formation of hydrochloric acid and separation of carbon, just as in the case of turpentine.

**Exp 105**—Fix a piece of candle into a deflagrating spoon, light it, and lower into a jar of chlorine. The candle continues to burn with a dull red smoky flame and soot is deposited on the walls of the jar.

Coal gas, again, consists almost entirely of a mixture of free hydrogen and compounds of carbon and hydrogen, and when a jet of lighted coal gas is lowered into a jar of chlorine it continues to burn, but the flame becomes duller and smoky owing to the separation of free carbon.

### 132. Combination of other Elements with Chlorine.—

**Exp. 106**—Into a jar of chlorine bring a piece of phosphorus on a deflagrating spoon and without the application of heat; presently the phosphorus will ignite and burn feebly with the formation of phosphorus trichloride—

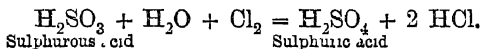


Antimony, copper and some other metals in a finely-divided condition also ignite when plunged into chlorine.

**Exp 107.**—Heat a piece of sodium in a deflagrating spoon until it takes fire, and then plunge it into a jar of chlorine, the sodium burns brilliantly, uniting with the chlorine to form sodium chloride.

**Inactivity of Dry Chlorine.**—It is found that, though, as we have seen, moist chlorine is a very active substance, *perfectly dry* chlorine is comparatively inactive. Thus, sodium even when heated does not combine with dry chlorine. Here, then, we meet with another example of the phenomenon already encountered in the case of hydrogen and oxygen, that the presence of water is necessary in order that a chemical reaction may take place.

**133 Oxidising Action of Chlorine.**—Chlorine is a strong oxidising agent *in the presence of moisture*, this property depending on its power of combining with the hydrogen of water and liberating *nascent* oxygen. An example of such action is its power of converting sulphurous acid into sulphuric acid.



Another example is furnished by the *bleaching* properties of chlorine, vegetable colouring matters, *e. g.* the pigments in the leaves and flowers of plants are deprived of their colour by moist chlorine, though in the absence of moisture no such action takes place.

**Exp 108.**—Prepare a jar of dry chlorine (using two sulphuric acid wash-bottles) Place in this a piece of cloth dyed with turkey-red and leave it some minutes with the cover on, no decolorisation will occur, but on moistening the cloth it will be bleached

**134. Action of Chlorine on Organic Substances.**—Many organic substances are very readily attacked by chlorine. In some cases (*e. g.* ethylene) the chlorine simply adds itself on to the compound, and *addition products* are formed. In other cases (*e. g.* marsh gas) chlorine replaces one or more atoms of hydrogen, and *substitution products* result: the

displaced hydrogen combines with more chlorine forming hydrochloric acid. We shall return to this subject when studying the hydrocarbons (see Chap XXII).

Chlorine is a very powerful *disinfectant*, as it rapidly kills the minute forms of life known as bacteria, which are the chief cause of the putrefaction of organic matter.

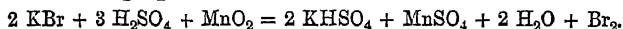
**135. Chlorine Hydrate.**—This substance is produced by passing chlorine into a mixture of water and ice. It is a greenish crystalline compound of uncertain composition, best represented by the formula  $\text{Cl}_2 \cdot x\text{H}_2\text{O}$ , where  $x$  is either 8, 9 or 10. At ordinary temperature it decomposes into chlorine and water.

**136. Liquid Chlorine**—Chlorine can readily be liquefied as described in § 29. Liquid chlorine is an orange-yellow substance of specific gravity 1.66; it boils at  $-33.6^\circ \text{C}$ . It is prepared commercially for use in extracting gold.

### BROMINE, $\text{Br}_2$ .

**\* 137. Occurrence.**—Bromine does not occur in the free state in nature. It is found in small quantities in combination with certain metals, chiefly potassium, sodium, magnesium and calcium, in sea water and in many mineral waters. The salt deposits of Stassfurt contain a small percentage of bromides, and it is from this source that most of the bromine of commerce is obtained.

**\* 138. Preparation.**—Bromine may be prepared from sodium bromide or potassium bromide by heating with strong sulphuric acid and manganese dioxide, just as chlorine is prepared from common salt.



**Exp. 109**—Introduce into a tubulated retort a mixture of about 20 grammes of potassium bromide and 10 grammes of manganese dioxide. Cover the mixture with strong sulphuric acid poured in through a funnel inserted in the tubulus of the retort. Insert the stopper and place over the open end of the retort a flask resting in a trough of water and covered over with a wet cloth, as shown in the

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\* The asterisked paragraphs and questions in this and the next chapter are not required for the London Matriculation Syllabus.



diagram (Fig 38). On gently heating the mixture bromine distils over and condenses in the cooled receiver, where it collects as a dark-red liquid. Since the vapours of bromine are very injurious, the operation *must* be performed in a fume cupboard with a *good draught*

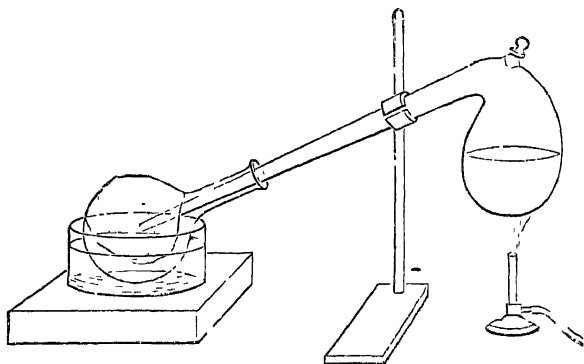


FIG 38.

\* 139. **Properties.**—Bromine is a heavy, mobile, dark-red liquid, possessing a very offensive odour (hence its name from  $\beta\rho\omega\mu\omicron\varsigma$  = a stench). Its action on the mucous membrane is worse even than that of chlorine. Bromine has a specific gravity of 3.188 (water = 1) at  $0^{\circ}\text{C}$ , and it boils at  $59^{\circ}\text{C}$ , the vapour possessing the same colour as the liquid. At ordinary temperatures bromine rapidly evaporates if exposed in an open vessel.

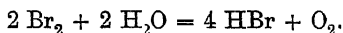
Bromine is soluble in a number of liquids giving reddish-brown solutions; the chief are—water, alcohol, ether, acetic acid, carbon disulphide, and chloroform. At  $0^{\circ}\text{C}$ . 1 gramme of water dissolves 0.036 grammes of bromine; the solubility in the other liquids mentioned is considerably greater.

**Exp. 110** —Test the solubility of bromine in some or all of the above liquids (using the bromine you prepared in the last experiment). By adding the bromine drop by drop to equal volumes of each of the liquids (say 5 c.c.), shaking up after each addition, and noting when further solution ceases (as shown by the bromine remaining undissolved at the bottom of the liquid), a rough comparison of its solubility in the different solvents can be made.

Bromine, like chlorine, contains two atoms in its gaseous molecule, except at high temperature, when partial dissociation into free atoms takes place. The dissociation is, however, much more complete with bromine than with chlorine.

As regards its chemical properties, bromine behaves like chlorine, but is generally much less active. Thus, many metals and non-metals combine readily with bromine, some (*e. g.* arsenic) with evolution of so much heat that they take fire. The action of bromine on phosphorus is, indeed, so violent that it is advisable to moderate it by dissolving the bromine in three times its volume of carbon bisulphide.

Bromine and hydrogen do not combine directly at ordinary temperature, but combination can be brought about by the application of heat, *e g* by passing the mixed gases through a red-hot tube. A solution of bromine in water (called *bromine water*) gradually decomposes in sunlight with evolution of oxygen and formation of hydrobromic acid—



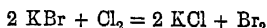
The decomposition is, however, much slower than with chlorine.

As we should expect from what has just been said, bromine water acts as a mild oxidising agent and exhibits feeble bleaching properties, its action being explained exactly as in the case of chlorine. It is much used as an oxidising agent in analytical chemistry. Bromine readily attacks organic substances such as starch and the skin, turning them *yellow*.

**Exp 111**—Add a drop of bromine water to some starch and note the yellow colour developed.

Bromine is readily displaced from its compounds with metals by the more active element chlorine. The following experiment should be performed to illustrate this.

**Exp. 112**—Add some chlorine water to a solution of potassium bromide. No red colour developed. Shake up the liquid with a little carbon disulphide. The bromine dissolves in it and the red solution collects at the bottom of the vessel.



Bromine is used in photography and in medicine, and also as a disinfectant.

**Bromine Hydrate.**—Bromine combines with water at low temperatures, forming a compound,  $\text{Br}_2 \cdot x\text{H}_2\text{O}$ , corresponding to chlorine hydrate.

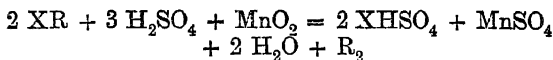
### IODINE, $\text{I}_2$ .

\* 140. **Occurrence** —Iodine is not found free in nature, but its compounds with the metals potassium, sodium, magnesium and calcium are widely distributed, though they do not occur in large quantity at any one place. Thus sea water and the plants and animals which inhabit the sea, notably sea-weed, contain small quantities of iodides, as also do many mineral waters. The crude sodium nitrate (caliche), found in such abundance in Chili and Peru, contains small quantities of sodium iodate, and this is now the chief source of the element.

\* 141. **Preparation.**—In the laboratory iodine is prepared in a similar manner to bromine, namely, by heating potassium or sodium iodide with manganese dioxide and strong sulphuric acid—



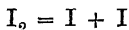
This method is, as we have seen, a general one for the preparation of the halogens, except fluorine, and the reaction may be represented thus—



where  $\text{X} = \text{K}$  or  $\text{Na}$  and  $\text{R} = \text{Cl}$ ,  $\text{Br}$  or  $\text{I}$ .

**Exp. 113.**—Prepare iodine by following the directions in Exp. 109, using potassium iodide in place of potassium bromide. The same apparatus should be used, but it will not be necessary to cool the receiver by cold water. Some of the iodine will probably condense in the neck of the retort, it can be driven into the receiver by gently warming with a Bunsen burner.

**\* 142. Properties.**—Iodine is a lustrous crystalline black solid of specific gravity 4.95. It melts at  $113^{\circ}\text{C}$ ., and boils at  $184^{\circ}\text{C}$ ., forming a deep violet vapour, at ordinary temperatures, however, iodine slowly undergoes vaporisation. The density of iodine vapour is very high, being about eight and a half times as great as that of air, and 126 times that of hydrogen. This corresponds to a molecular weight of  $2 \times 126 = 252$ , which is about twice the atomic weight of iodine, so that the gaseous molecule of iodine contains two atoms. This is only true up to  $450^{\circ}\text{C}$ ., however, for above this temperature the density gradually falls, till at  $1,500^{\circ}\text{C}$ . its value is reduced by nearly one-half, showing that most of the molecules have been broken down into single atoms—



We have seen that chlorine and bromine behave in a similar manner, but the decomposition is much less complete than in the case of iodine. Since bromine is decomposed to a greater extent than chlorine, we have here another property which follows the order of the atomic weights of the three elements.

Iodine is only slightly soluble in water, 100 grammes of which dissolve 0.02 gramme of the element, but many other liquids dissolve it in much greater quantity. These solvents may be divided into two classes, according as the colour of the solution they produce is reddish-brown or violet; to the former class belong water, potassium iodide, alcohol, and ether; and to the latter, carbon disulphide, chloroform, and liquid hydrocarbons.

**Exp 114.**—Introduce a crystal of iodine into about 5 c.c. of each of the liquids mentioned above (as an example of a liquid hydrocarbon you can use benzene). You will notice that in all these liquids, except water, a deeply-coloured solution is rapidly formed; the water is only coloured slightly brown.

Observe that the colours of the different solutions correspond with those stated above.

**\* 143. Action of Iodine on other Elements.**—Iodine is not nearly such an active substance as the other halogens, but it nevertheless combines directly with many elements, both

metals and non-metals, often, indeed, without the application of heat. For example, mercury and iodine will unite on merely rubbing them together; again, on bringing together phosphorus and iodine, the phosphorus first melts and then combination takes place with so much energy that the mixture bursts into flame. When antimony powder is thrown into iodine vapour it takes fire, and on heating potassium and iodine together they unite with explosive violence.

Hydrogen and iodine combine directly with even greater difficulty than hydrogen and bromine, the temperature necessary being much higher; the combination is facilitated by the presence of spongy platinum, which acts as a catalytic agent. As we should expect from this, iodine in the presence of water has no bleaching properties.

**\* 144. Displacement of Iodine from its Salts.**—Just as chlorine displaces bromine from its compounds, illustrating thereby its greater activity, so both chlorine and bromine will displace iodine from its compounds. For example, on treating potassium iodide with either chlorine or bromine, free iodine is liberated—



**Exp. 115.**—Add a few drops of chlorine water to about 10 c.c. of a solution of potassium iodide. The solution will turn reddish-brown, owing to the liberated iodine dissolving in the excess of potassium iodide. Now shake up with a little carbon bisulphide. This will dissolve out the iodine, forming a violet solution which will collect at the bottom of the vessel.

A similar experiment may be performed using bromine water in place of chlorine water.

**\* 145. The "starch test" for Iodine.**—Iodine forms a very characteristic blue compound with starch. On heating, the compound is decomposed and the colour disappears, but on cooling recombination takes place and the colour reappears.

**Exp 116**—Shake a very little starch in a test-tube of cold water and boil well; add a few drops of a solution of iodine in potassium iodide; a blue colour is formed. Boil the blue solution, and the blue colour disappears, reappearing on cooling.

**146. Uses.**—Iodine is largely employed in medicine for taking down glandular swellings. It was at one time thought that the iodine must be applied in the free state, and an alcoholic solution was (and still is) used; it has recently been found, however, that potassium iodide is quite as effective, and as it does not leave any stain on the skin its employment is preferable.

Iodine in the form of potassium iodide is also used as a tonic. Further, a compound of iodine with carbon and hydrogen, called iodoform ( $\text{CHI}_3$ ), finds wide application as an antiseptic.

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### QUESTIONS.—CHAPTER XIV.

1. Draw up in tabular form a comparison between the halogen elements with regard to—(a) their colour, (b) their solubility in water, (c) their action on water, (d) their affinity for hydrogen.
2. Describe how you would prepare and collect a jar of dry chlorine. Sketch the apparatus you would employ.
3. Describe experiments illustrating the great affinity of chlorine for hydrogen.
4. Describe the chemical changes which accompany the burning of a candle in chlorine, and show how far they account for the peculiar appearance of the flame which is observed when a candle burns in chlorine.
5. Describe experiments illustrating the *oxidising action* of chlorine.
6. Under what conditions does chlorine act as a bleaching agent?

7. Describe exactly how you would prepare bromine from potassium bromide, and give a sketch of the apparatus you would employ.
8. Name some liquids which dissolve bromine and iodine, and state the colour of the solution produced in each case. Compare the action of these two halogens on starch.
9. What is the action of chlorine on solutions of sodium bromide, potassium iodide and sulphuretted hydrogen respectively?
- \*10. Describe the action, if any, which takes place when sulphur, phosphorus, carbon, silicon and sulphuretted hydrogen are respectively brought into contact with iodine.
11. By what general method can the halogens (except fluorine) be prepared?

## CHAPTER XV.

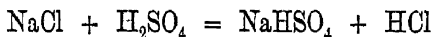
### COMPOUNDS OF HYDROGEN WITH THE HALOGENS.

147. HYDROGEN forms one compound with each of the halogens. These compounds are all gases at the ordinary temperature, except hydrogen fluoride, which is a very volatile liquid. They are all very soluble in water, producing strongly acid solutions. It will be convenient, for purposes of terminology, to use the terms *hydrogen fluoride*, *hydrogen chloride*, etc., for the gaseous acids (or anhydrous liquids), reserving the expressions *hydrofluoric acid*, *hydrochloric acid*, etc., for the aqueous solutions of the hydrides.

#### HYDROGEN CHLORIDE OR HYDROCHLORIC ACID, HCl.

148. **Occurrence.**—Hydrogen chloride is one of the gaseous products of the eruption of volcanoes.

**Preparation.**—Hydrogen chloride is most conveniently prepared by the action of concentrated sulphuric acid on common salt (sodium chloride).\* The gas is evolved in the cold with effervescence, but much more rapidly on gently heating; the following reaction takes place—



Hydrogen chloride cannot be collected over water, in which it is very soluble, it may however be collected by downward displacement of air or over mercury.

\* All chlorides except silver chloride and mercurous chloride yield hydrochloric acid when heated with sulphuric acid.



**Exp. 117.**—The apparatus required for the preparation of hydrogen chloride is sketched in Fig. 39. Introduce into the flask some common salt, and fill the wash-bottle about one-third full of concentrated sulphuric acid. Connect up the apparatus as shown and pour concentrated sulphuric acid slowly down the thistle funnel till it just covers the salt. Warm *gently* and collect the gas, which is dried by the sulphuric acid in the wash-bottle, in glass cylinders or other vessels as required. If the gas is wanted *pure* and *quite dry* it should be passed through two sulphuric acid wash-bottles and collected over mercury.

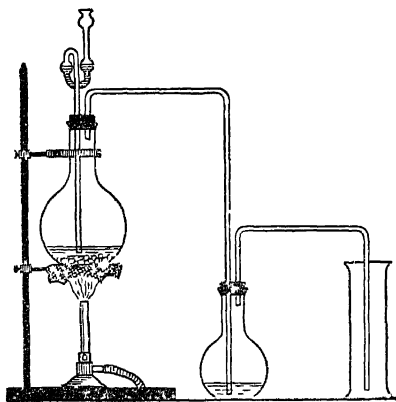


FIG. 39.

**149. Properties.**—Hydrogen chloride is a colourless gas which fumes in moist air and has a strongly irritant action on the mucous membrane. Its density is 18.2 ( $H = 1$ ), and it is therefore about  $1\frac{1}{2}$  times as heavy as air.

Hydrogen chloride is extremely soluble in water, 1 c.c. of which at  $0^{\circ} C$  dissolves 503 c.c. of the gas, and at ordinary temperatures about 450 c.c. The solution of the gas is accompanied by a considerable evolution of heat, and there is also an increase in the volume of the liquid. The following experiment illustrates in a striking manner the great solubility of hydrogen chloride.

**Exp. 118** —Fill a large dry flask, of at least two or three litres content, with hydrogen chloride gas by displacement. Fit it with an

india-rubber cork, through which passes a tube with stopcock, and drawn out into a jet as shown in Fig 40. Dip the extreme end of the tube into water and open the stopcock.

Under these conditions the gas at first only comes into contact with the water very slowly by a process of diffusion, and it is desirable to bring about contact with a larger surface of water by cooling the flask, this may be done by pouring a few drops of ether over its surface. When the water reaches the top of the tube and overflows into the flask, the first few c. c. of water dissolve the whole of the gas, and the rest of the water rushes up through the tube with great force to fill the vacuum in the flask.

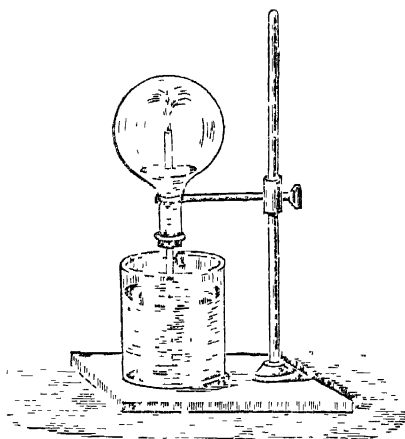


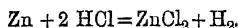
FIG 40

Hydrogen chloride is not combustible nor is it a supporter of combustion.

**Exp 119.**—Introduce a lighted taper into a jar of the gas. The flame is extinguished and the gas does not burn. Try similar experiments with burning sulphur and phosphorus; these are also extinguished.

The gas attacks many metals, especially when heated, with liberation of hydrogen and formation of a chloride of the metal.

**Exp. 120.**—Place some zinc in a short piece of combustion tubing, heat it, and pass hydrogen chloride over it. Collect the gas given off over water. Test it with a lighted taper, it is hydrogen. The white residue left in the tube is zinc chloride,  $\text{ZnCl}_2$ .

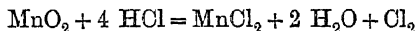


Similar experiments may be performed with other metals, *e.g.* iron and magnesium.

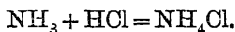
Hydrogen chloride also reacts with many metallic oxides, especially when heated. If the oxide is a *basic oxide*, water and a chloride of the metal are the products; an experiment (Exp. 86) illustrating this has already been performed, *peroxides*, on the other hand, give rise to free chlorine, together with water and a chloride of the metal.

**Exp. 121.**—Proceed exactly as described in Exp. 86, using manganese dioxide instead of lime. Test the issuing gas, which is yellowish-green in colour, with moist litmus paper, it is bleached. The gas is chlorine.

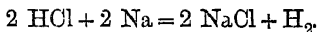
The equation representing the change which takes place is the same as that we have already met with in the preparation of chlorine, *viz.*—



When the gas is brought into contact with ammonia gas direct combination takes place with formation of dense white fumes of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) unless the gases are *quite dry*—



**150 Analytical proof of the Composition of Hydrogen Chloride**—We can prove that hydrogen chloride contains half its volume of hydrogen by acting on it with metallic sodium, when the chlorine is extracted and combines with the sodium forming sodium chloride—



The sodium is most conveniently used in the form of a

solution in mercury (called *sodium amalgam*), and the experiment may be carried out as follows:—

**Exp. 122.**—About 50 c.c. of hydrogen chloride are introduced into the closed limb of a bent eudiometer tube previously filled with mercury (Fig 41). The levels of mercury in the two limbs are made equal by running mercury out of the tap or pouring more into the open limb, and the volume of gas is measured. Mercury is now allowed to run out of the tap till very little is left in the open limb and the latter is filled up with liquid sodium amalgam. The open end is then closed by the thumb and the hydrogen chloride transferred to the other limb by inverting and suitably manipulating the apparatus. The eudiometer is now restored to its normal position and then again inverted

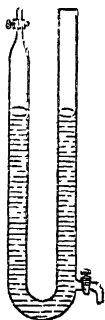


FIG. 41.

so as to bring the gas intimately in contact with the amalgam. Finally the gas is restored to the closed limb, and liquid is run out through the tap till the levels in the two limbs are equal. The volume of gas which remains will be found to be half that originally taken, and it may be proved to be hydrogen by the usual tests.

To prove that the volumes of chlorine and hydrogen which combine to form hydrogen chloride are equal, an aqueous solution of the gas may be submitted to electrolysis

**Exp 123**—The experiment is carried out in the apparatus shown in Fig. 42, which consists of a three-limbed glass vessel, the two side limbs being provided with stopcocks and the central one with a funnel. At the base of the side limb are the electrodes which are connected to the poles of a battery. The negative electrode, at which hydrogen is evolved, may be made of platinum, but since chlorine acts on platinum the positive electrode must

be made of gas carbon. Strong hydrochloric acid is introduced through the funnel till the side tubes are full, and an electric current is passed through the liquid with the stopcocks open till the liquid in the limb containing the positive electrode is saturated with chlorine; the hydrogen liberated in the other limb being almost insoluble escapes meanwhile through the open stopcock. The stopcocks are now closed, and the gases will be found to collect in equal volumes in the two limbs. Their identity may be proved by the usual tests.

From the results of these two experiments it follows that two volumes of hydrogen chloride consists of one volume of hydrogen and one volume of chlorine.

**151. Synthetical proof of the Composition of Hydrogen Chloride.**—The composition of hydrogen chloride may be conveniently investigated synthetically by means of the following experiment:—

**Exp. 124.**—Hydrochloric acid is electrolysed in the vessel A, Fig 43 (using gas carbon electrodes), and when the liquid is saturated with chlorine a stout glass tube B, provided with a stopcock at each end, is attached to the delivery tube of A. The other end of B is connected with a bottle containing fragments of pumice stone moistened

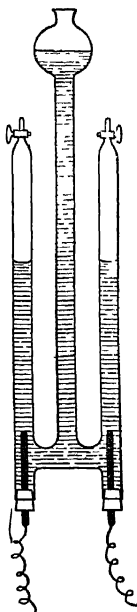


FIG. 42.

with caustic soda solution to absorb the chlorine as it escapes. The stopcocks are opened and the mixture of hydrogen and chlorine in equal volumes generated in A is passed through B for some time so that all the air is driven out.\* The stopcocks are then closed and the tube disconnected.

On opening one of the stopcocks under a solution of potassium iodide the chlorine reacts with the KI, liberating iodine, and if the experiment has been conducted properly

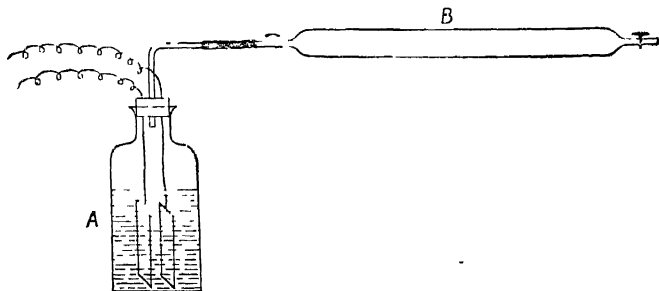


FIG 43.

the liquid will rise just half-way up the tube, showing that the chlorine and hydrogen are present in equal volumes. The tube is now cleaned out and again filled with the electrolytic mixture of hydrogen and chlorine. The stopcocks are again closed and the tube is disconnected and exposed to the action of the rays from burning magnesium wire (the face should be protected by a thick sheet of glass to avoid accident in case the tube explodes). The gases combine with explosion. The tube is allowed to become quite cold and one of the stopcocks is then opened under mercury. No gas escapes and the mercury does not rise in the tube, showing that the volume of hydrochloric acid

\* This must be done in the dark to prevent combination of the gases,

is exactly the same as that of the mixed gases from which it was formed. The stopcock is now closed and opened again under water, the water rushes up and fills the whole tube, the hydrogen chloride formed dissolving completely. This shows that the whole of the gases have combined to form hydrogen chloride. We thus arrive at the same composition for hydrogen chloride by synthesis as by analysis.

**152. Liquid Hydrogen Chloride.**—Hydrogen chloride condenses to a colourless liquid under a pressure of 40 atmospheres at  $10^{\circ}\text{C}$ .; the liquid boils under ordinary pressure at  $-83.7^{\circ}\text{C}$ . Liquid hydrogen chloride is without action on most metals, *e.g.* magnesium and zinc, nor does it act on metallic oxides, such as lime, or on anhydrous carbonates; it is therefore an inactive substance.

**153. Preparation of Aqueous Hydrochloric Acid.**—A solution of hydrogen chloride in water, commonly called hydrochloric acid (also known as “spirits of salts” and “muriatic acid”), may be conveniently prepared in the following manner:—

**Exp. 125.**—Generate hydrogen chloride in the flask A (Fig 44), as described in Exp. 117, and pass the gas through an *empty* wash-bottle B, arranging so that the delivery tube of A reaches just below the cork of B. Lead the gas away by a delivery tube which reaches to the bottom of B and is connected by rubber tubing with a wider tube dipping in a beaker of water. The hydrogen chloride is absorbed by the water, and if the process is continued long enough the solution finally becomes saturated, when it contains from 40–45 % of HCl.

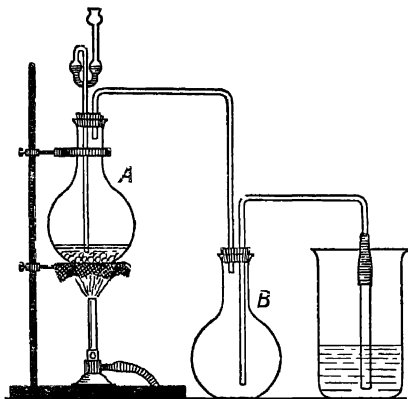


FIG 44.

The object of the empty wash-bottle is to guard against any accident owing to a sudden cessation in the evolution of the gas which, owing to the great solubility of hydrogen chloride, would result in a reduction of pressure in the apparatus and consequent "sucking back" of the liquid in the beaker. If no wash-bottle were present the liquid would be sucked back into the generating flask, but with the arrangement described it merely passes into the empty wash-bottle. Further, by arranging the delivery tubes in the wash-bottle as shown, it is impossible for the liquid to pass back out of the wash-bottle into the generating flask, even if it is all sucked out of the beaker into the wash-bottle; all that will happen if the gas in the apparatus is still under reduced pressure will be that air will be drawn in through the delivery tube in the beaker, and will bubble through the liquid now present in B, and mix with the hydrochloric acid above this liquid till the pressure is atmospheric.

**154. Properties of Aqueous Hydrochloric Acid.**—Hydrochloric acid is a strongly acid liquid turning blue litmus a bright red; it is very corrosive, being much more active than the gas.

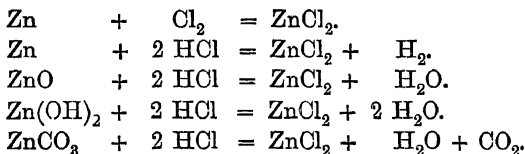
**Action on Metals.**—Many metals are attacked by hydrochloric acid, some readily by the dilute acid, others only by the hot concentrated acid. In all cases the products are a chloride of the metal and hydrogen. The following table gives a *résumé* of the action of the acid on a number of common metals under different conditions.

Metal.	Cold dilute HCl	Hot conc. HCl.
Zinc	Dissolves readily	Dissolves readily
Magnesium	" "	" "
Iron	" "	" "
Aluminium	" rather slowly	" "
Tin	" slowly	" "
Copper	Insoluble*	" slowly
Lead	"	" very slowly
Mercury	"	Insoluble
Silver	"	"
Gold	"	"
Platinum	"	"

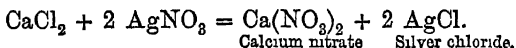
\* Copper is slowly attacked by dilute hydrochloric acid *in the presence of air*; the same remark applies to lead.



**155. Chlorides.**—The chlorides of the metals may be produced by the direct union of the metals with chlorine, or by the action of hydrochloric acid on the metals (in some cases) or on their oxides, hydroxides or carbonates. Zinc chloride,  $\text{ZnCl}_2$ , for instance, may be produced by any of these methods as shown in the following equations:—



When a metal forms an *insoluble* chloride a special method of preparation is applicable, viz. the addition of a solution of a soluble chloride to a solution of soluble salt of the metal, double decomposition takes place, the insoluble chloride being precipitated. Silver chloride is, for example, precipitated when a solution of silver nitrate,  $\text{AgNO}_3$ , is added to a solution of calcium chloride,  $\text{CaCl}_2$ .

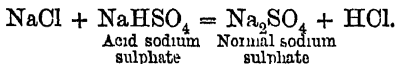


Most metallic chlorides are easily soluble in water; the only insoluble ones are mercurous chloride (calomel),  $\text{HgCl}$ , cuprous chloride,  $\text{Cu}_2\text{Cl}_2$ , lead chloride,  $\text{PbCl}_2$  (which is sparingly soluble in cold water and readily in hot) and aurous chloride,  $\text{AuCl}$ , in addition to silver chloride already referred to.

**156. Action of Heat on Hydrochloric Acid.**—When a strong solution of hydrochloric acid is distilled it at first loses hydrochloric acid much faster than water, i.e. it becomes weaker. This goes on till the percentage of  $\text{HCl}$  is 20·24, when the liquid distils over unchanged in composition. Similarly, if a solution containing less than 20·24 per cent. of hydrochloric acid is distilled it loses water faster than  $\text{HCl}$  till the percentage of  $\text{HCl}$  is 20·24, when the liquid again distils unchanged. The boiling-point of

hydrochloric acid of this particular strength is  $110^{\circ}\text{C}$ . It must be noted that the acid which distils unchanged only has the composition and boiling-point stated when the *pressure is normal*, for any other pressure, the composition and boiling-point of the liquid which distils unchanged have different values, which, however, are constant for each particular pressure.

**157. Manufacture of Hydrochloric Acid.**—Hydrochloric acid is manufactured in enormous quantities as a by-product in the conversion of common salt into salt-cake (sodium sulphate,  $\text{Na}_2\text{SO}_4$ ) by the action of strong sulphuric acid. The first part of the process is performed at a gentle heat and the reaction is the same as that given in § 148. The mixture is then heated to a *much higher* temperature, when the acid sodium sulphate reacts with another molecule of sodium chloride, producing normal sodium sulphate and hydrochloric acid according to the equation—



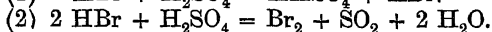
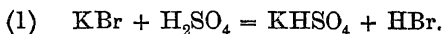
The gas is passed up stone towers filled with lumps of coke, over which a slow stream of water flows; the hydrochloric acid is absorbed, and the aqueous solution runs away from the bottom of the tower into suitable receivers.

**Impurities in the Commercial Acid.**—The chief impurities in commercial hydrochloric acid are ferric chloride, free chlorine, sulphuric acid, arsenious chloride, and sulphurous acid. The ferric chloride is the principal cause of the yellow colour usually noticeable in the commercial acid.

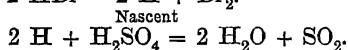
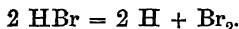
**158. Uses of Hydrochloric Acid.**—The most important use of hydrochloric acid is in the manufacture of chlorine. It is also used in dyeing and calico printing, in obtaining phosphates from bones, and in manufacturing colours. Its employment in the manufacture of metallic chlorides is also of importance, and it is very extensively used in chemical laboratories for a variety of purposes.

## HYDROGEN BROMIDE OR HYDROBROMIC ACID, HBr.

\* 159 Preparation.—Hydrogen bromide cannot conveniently be prepared from potassium or sodium bromide in the same way that hydrogen chloride is prepared from common salt, because some of the product undergoes a secondary reaction with sulphuric acid, reducing it to sulphurous acid with liberation of free bromine.



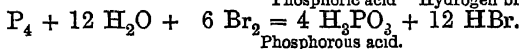
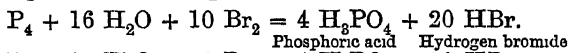
This reducing action is a result of the instability of hydrogen bromide, which readily splits up into free hydrogen and bromine, the nascent hydrogen so produced then attacking the sulphuric acid thus—



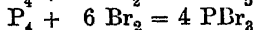
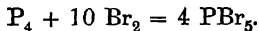
These two equations when combined give equation (2) above.

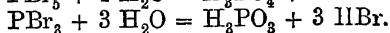
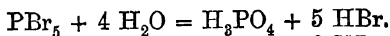
If, instead of sulphuric acid, an acid such as phosphoric acid, which is not so easily reduced, is employed, then the preparation can be carried on just as for hydrogen chloride.

The best method of preparation is to drop bromine on to a mixture of amorphous phosphorus and water, when the following reactions take place—



The particular reaction which preponderates depends on the relative quantities of phosphorus and bromine used. It may be supposed that these reactions take place in two stages, phosphorus and bromine first uniting to form phosphorus pentabromide ( $\text{PBr}_5$ ) and phosphorus tribromide ( $\text{PBr}_3$ ), these compounds being immediately decomposed by water, thus—





The experiment is carried out as follows —

A mixture of one part of amorphous phosphorus and

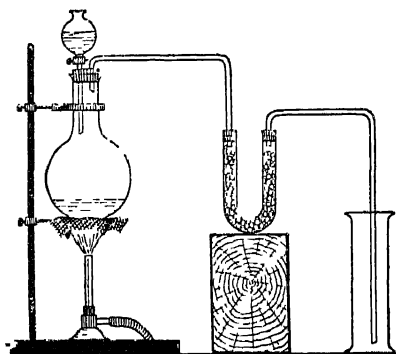


FIG. 45.

ten parts of water is introduced into a flask provided with a dropping funnel and delivery tube, as shown in Fig. 45. Ten parts of bromine are introduced into the funnel, and are *gradually* run into the flask, this is then *gently* warmed, and the hydrogen bromide is passed through a U-tube containing lumps of amorphous

phosphorus to remove bromine, the gas being collected by downward displacement or over mercury. Like hydrogen chloride, it cannot be collected over water, owing to its great solubility. If an aqueous solution of the gas is required, the delivery tube from the U-tube in Fig. 45 should be connected with a wash-bottle and beaker of water as shown in Fig. 44. An even more convenient method of absorbing the gas (which can be used for any very soluble gas) is to connect the delivery tube from the U-tube with a funnel which reaches to *just above*\* the surface of some water in a beaker as

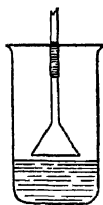
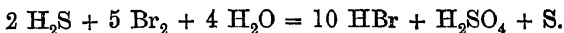


FIG. 46.

\* A variation of the method is to have the rim of the funnel *just below* the surface of the water. If the liquid "sucks back" its level in the beaker soon falls below the rim of the funnel, after which no more liquid can leave the beaker.

shown in Fig. 46. The hydrogen bromide is absorbed as fast as it reaches the water, and practically none of it escapes

Another simple method of preparing a solution of the gas is to pass sulphuretted hydrogen into bromine water, when the following change takes place:—



The precipitate of sulphur is filtered off and the liquid distilled, when hydrobromic acid passes over and sulphuric acid remains behind.

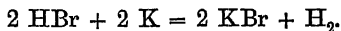
**\* 160. Properties.**—Hydrogen bromide is a heavy colourless gas which, like hydrogen chloride, fumes in moist air, and has an irritating action on the mucous membrane. As already stated it is very soluble in water, producing a strongly acid solution which is very similar in properties to hydrochloric acid.

On distilling hydrobromic acid at normal pressure it loses either water or acid, according as the solution contains less or more than 48·17 per cent. of HBr. The liquid of this composition distils over unchanged at 126° C. If the pressure is not normal there is a corresponding change in the composition and boiling-point of the liquid which distils unchanged.

Hydrogen bromide is incombustible, and is a non-supporter of combustion. It is immediately attacked by chlorine with liberation of free bromine and formation of hydrogen chloride—



Potassium, on the other hand, immediately liberates free hydrogen from hydrogen bromide, and forms potassium bromide—

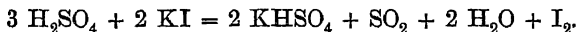


**\* 161. Bromides.**—The general methods of preparation of metallic bromides are similar to those given for metallic chlorides. Most metallic bromides are readily soluble in water, the only common insoluble ones being silver bromide

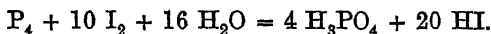
(AgBr), mercurous bromide (HgBr), and lead bromide (PbBr<sub>2</sub>), the last being sparingly soluble in cold water, but readily in hot water.

### HYDROGEN IODIDE OR HYDRIODIC ACID, HI.

**\* 162 Preparation.**—Hydrogen iodide cannot be prepared by the action of sulphuric acid on potassium or sodium iodide for a reason similar to that given in the case of hydrogen bromide; hydrogen iodide is, in fact, much more unstable than hydrogen bromide, and the reaction goes almost entirely in accordance with the equation—



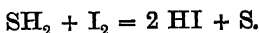
If phosphoric acid is used, however, instead of sulphuric acid, hydrogen iodide is obtained free from iodine just as hydrogen bromide could be obtained free from bromine. Hydrogen iodide is best prepared by a method similar to that used for hydrogen bromide, namely, by the mutual interaction of phosphorus, iodine and water. The apparatus used is that shown in Fig. 45; since iodine is a solid it cannot be run in from a stoppered funnel as bromine is; instead, the iodine and amorphous phosphorus are mixed in the flask, and water is slowly run in from the funnel. Hydrogen iodide is evolved without heating, and, after passing through the U-tube containing amorphous phosphorus which removes iodine vapour, is collected by downward displacement or over mercury. When all the water has been added and the evolution of gas becomes slow the flask may be gently warmed. The reaction which takes place is thus represented—



If an aqueous solution of the gas (called hydriodic acid) is required, the absorption may be carried out by one of the methods described for HBr, as HI is also very soluble in water.

Another convenient method for the preparation of

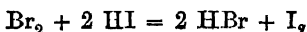
hydriodic acid is to pass sulphuretted hydrogen through water containing iodine in suspension, when the following change takes place:—



The hydriodic acid is separated from the precipitate of sulphur by distillation.

\* 163. **Properties**—Hydrogen iodide is a very heavy colourless gas which, like the other halogen hydrides, fumes strongly in moist air and has a very irritating action on the mucous membrane. Its great solubility in water has already been referred to; the aqueous solution has strongly acid properties just like the solution of the other halogen hydrides. The behaviour of the solution on distillation is exactly similar to that of hydrochloric acid and hydrobromic acid; the liquid which distils unchanged at normal pressure contains 57·7 per cent. of hydrogen iodide and boils at 127° C, but at other pressures the composition and boiling-point have different values. Hydrogen iodide is easily condensed to a liquid, a pressure of four atmospheres at 0° C. sufficing to bring this about; the liquid boils at -34·1° C. under normal pressure. Hydrogen iodide does not burn nor does it support combustion. As already pointed out, it is an unstable substance, thus on exposing the gas to sunlight it slowly undergoes decomposition into its elements, and on heating it breaks up much more quickly. Also the aqueous solution gradually turns brown in sunlight owing to separation of free iodine. On account of its instability and consequent tendency to produce nascent hydrogen, hydriodic acid is a powerful reducing agent, and is much used as such in organic chemistry; we have already had occasion to notice its reducing action on strong sulphuric acid.

Hydrogen iodide, both in the gaseous state and in aqueous solution, is at once decomposed by chlorine or bromine with liberation of free iodine—



\* 164. **Iodides**—The iodides of the metals are produced by methods similar to those given for chlorides and bromides. The majority of the iodides dissolve easily in water, the chief insoluble ones being silver iodide ( $\text{AgI}$ ), mercurous iodide ( $\text{HgI}$ ), mercuric iodide ( $\text{HgI}_2$ ), cuprous iodide ( $\text{Cu}_2\text{I}_2$ ), and lead iodide ( $\text{PbI}_2$ ), the last being sparingly soluble in cold water and readily in hot.

\* 165 **Tests for the Halogen Acids and their Salts.**

(1) A solution of silver nitrate,  $\text{AgNO}_3$ , when added to a solution of a halogen acid or haloid salt, gives with

*Hydrochloric acid*, a white curdy precipitate of silver chloride,  $\text{AgCl}$ , soluble in ammonia, insoluble in nitric acid.

*Hydrobromic acid*, a pale yellow precipitate of silver bromide,  $\text{AgBr}$ , soluble in strong ammonia, insoluble in nitric acid.

*Hydriodic acid*, a yellow precipitate of silver iodide,  $\text{AgI}$ , insoluble in ammonia and nitric acid.

(2) Free  $\text{HCl}$ ,  $\text{HBr}$ , or  $\text{HI}$ , heated with manganese dioxide, or their salts, heated with manganese dioxide and sulphuric acid, evolve chlorine, bromine and iodine respectively, and these elements are easily recognised by their colour, smell and bleaching action.

(3) Chlorine water (which must not be in excess) added to a bromide or iodide liberates bromine or iodine, and on shaking the liquid with carbon bisulphide, the bromine imparts to it a red colour and the iodine a violet colour.

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### QUESTIONS.—CHAPTER XV.

1. How would you prepare *pure dry* hydrogen chloride? Describe experiments which illustrate the chief properties of the gas.
2. State the changes which take place when very concentrated and very dilute hydrochloric acid are respectively boiled for some time in an open vessel.



3. On what evidence do we accept  $\text{HCl}$  as expressing the composition of hydrochloric acid gas?
4. Compare the properties of liquid hydrogen chloride with those of an aqueous solution of the gas.
5. What is the action (if any) of (a) cold dilute, (b) hot strong hydrochloric acid on the following metals. (1) zinc, (2) aluminium, (3) gold, (4) lead, (5) copper, (6) tin?
6. State briefly the general methods of preparing metallic chlorides, giving equations.
7. How is hydrochloric acid manufactured? What are the chief impurities in the commercial acid?
8. Enumerate the chief uses of hydrochloric acid.
- \*9. Describe in detail the laboratory method of preparing an aqueous solution of hydrobromic acid.
- \*10. Describe a method of preparing gaseous hydriodic acid. In what respects do hydriodic acid and hydrochloric acid resemble each other, and in what respects do they differ?

## CHAPTER XVI.

### NITROGEN—THE ATMOSPHERE—AMMONIA.

#### NITROGEN, $N_2$

166. NITROGEN is the first member of a group of elements, nitrogen, phosphorus, arsenic, antimony and bismuth, which either in themselves or their compounds exhibit considerable analogy to one another. The first two members only are usually classed with the non-metals.

The elements forming this group show a transition in physical properties as the atomic weight increases, nitrogen being gaseous at the ordinary temperature, whilst phosphorus is solid but easily vaporised, the other members being more difficult to volatilise

Speaking more particularly with regard to nitrogen and phosphorus, it will be seen by a reference to the following pages that they resemble one another —

(1) In forming hydrides of similar composition  $NH_3$ ,  $PH_3$ , both of which combine directly with haloid acids yielding the ammonium and phosphonium salts

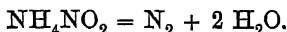
(2) In forming a characteristic series of oxides some of which yield powerful acids

167. **Occurrence** — Nitrogen occurs mixed with oxygen in the atmosphere, of which it forms nearly four-fifths the volume

Although it does not enter to any large extent into the composition of animal and vegetable tissues, it is, notwithstanding, a very constant and essential constituent of such

tissues. The nitrogen of plants is obtained chiefly through the medium of the soil, in which small quantities of nitric acid, nitrates and ammonium salts always occur. Animals cannot assimilate nitrogen directly, and derive their supply from the plants.

**168. Preparation.**—We have seen in Experiments 18 and 19 that air may be deprived of its oxygen by means of iron or phosphorus. The most convenient method of bringing this about in practice is to pass air over heated copper contained in a hard glass tube. The nitrogen so obtained is not pure, for air contains a number of other inert gases, chiefly argon, in addition to nitrogen (see § 179). The best method of preparing pure nitrogen is to heat a solution of ammonium nitrite—

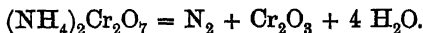


In practice a mixture of ammonium chloride,  $\text{NH}_4\text{Cl}$ , and sodium nitrite,  $\text{NaNO}_2$ , is used instead of ammonium nitrite, since both  $\text{NH}_4\text{Cl}$  and  $\text{NaNO}_2$  are common salts, whereas  $\text{NH}_4\text{NO}_2$  is an unstable compound. We may suppose that the  $\text{NH}_4\text{Cl}$  and  $\text{NaNO}_2$  undergo double decomposition with formation of  $\text{NH}_4\text{NO}_2$  and  $\text{NaCl}$ , and that the ammonium nitrite is then decomposed according to the equation given above.

**Exp 126** —Introduce about 15 grammes of sodium nitrite and 10 grammes of ammonium chloride into a small flask, and add about 100 c.c. of water. Fit the flask with a cork carrying a delivery tube. Warm gently and collect the nitrogen over water at the pneumatic trough.

If the nitrogen is required dry, it should be passed through a sulphuric acid wash-bottle and collected over mercury.

Another method of preparation is to heat ammonium bichromate  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ .



Instead of ammonium bichromate, it is more convenient to use a mixture of ammonium chloride and potassium



171. **Determination of the Composition of the Atmosphere by Volume**—A rough method of determining the volumetric composition of the atmosphere has already been described in Exp 19. A better method is to explode a known volume of air with about twice its volume of hydrogen in a eudiometer; two volumes of hydrogen combine with one volume of oxygen to form water vapour, which condenses, and thus *one-third* the diminution in volume represents the volume of oxygen present. This method is not quite accurate, because some of the nitrogen and oxygen combine to form nitrogen peroxide, which

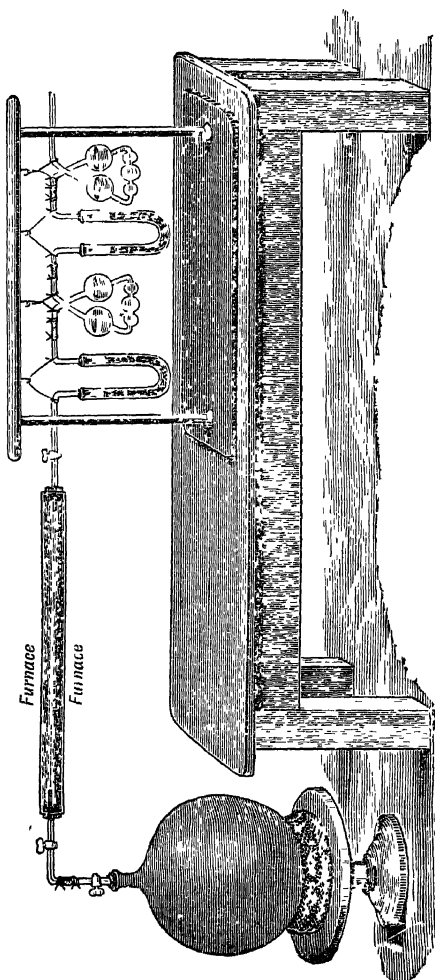


FIG 47

dissolves in the water produced with formation of nitric and nitrous acids

172. **Determination of the Composition of the Atmosphere by Weight.**—This may be ascertained by passing the air over red-hot copper, with which the oxygen combines, as in the experiment just described.

The air is previously freed from carbon dioxide and moisture by being passed over potash and concentrated sulphuric acid. The apparatus used is shown in Fig 47, it consists essentially of a large glass globe, to which is attached a tube containing metallic copper, and heated in a furnace. The globe is first rendered vacuous by means of a good air-pump, the stopcock is closed, and the globe carefully weighed. The tube containing the copper is then rendered vacuous, closed and weighed. The copper having been heated to redness, the stop-cock is opened sufficiently to allow a slow current of purified air to pass through the tube and into the glass globe. On the way, it is deprived of its oxygen, and if the experiment has been carefully conducted, only nitrogen and argon pass into the globe. After the apparatus has quite cooled, the globe is again weighed, and the increment gives *the weight of the nitrogen and argon*. The tube is also weighed again, and the increase there shows *the weight of the oxygen*, together with a little nitrogen and argon which remain in the tube. On exhausting and weighing again, the decrease in weight is added to the increase in weight of the globe to obtain the total nitrogen and argon. The oxygen is given by the difference of the two weighings of the *exhausted* tube.

A series of such determinations gave the composition by weight of air as—

Nitrogen and argon	...	...	...	76.995
Oxygen	...	...	...	23.005.

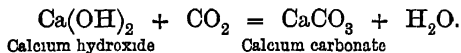
173. **Water Vapour in Air.**—The amount of water vapour varies with the temperature and the degree of saturation of the air, for the higher the temperature of the air, the more moisture will it take up before it is saturated.

The average amount is somewhat under 1 per cent by volume, but in warm, moist climates may approach 4 per cent. It may be measured by observations on the dew-point (see text-books on physics), or by passing a known volume of air over calcium chloride contained in U-tubes, and noting the increase in weight of the tubes.

The amount of water vapour which the air can contain may be estimated by the fact that 1 cubic mile of air saturated at 35° would deposit, if cooled to 0°, 140,000 tons of rain. But while the air is seldom completely saturated, it never contains less than  $\frac{1}{10}$  of the possible amount.

**174 Carbon Dioxide in Air.**—The amount of this gas in air varies considerably, according to the locality from which the sample of air is taken. In country air there are from three to four volumes of  $\text{CO}_2$  in 10,000, but in towns the amount is larger, and may reach seven or eight volumes. In badly-ventilated dwellings even ten-fold the normal amount of carbon dioxide may occur. The determination of carbon dioxide is a matter of importance, especially in the case of indoor air, since it serves to show the efficiency of ventilation.

The presence of carbon dioxide in air may be shown by exposing lime-water in a shallow dish, the lime-water is soon covered with a thin pellicle, owing to the formation of calcium carbonate or chalk, which is insoluble in water—



Baryta water may, by Pettenkofer's method, be used as a means of determining the amount of carbon dioxide in air. A known volume of a solution of baryta (which is alkaline) of known strength is shaken up with a measured quantity of air, say 10 litres; part of the baryta is converted into barium carbonate (a neutral body), whilst part remains unaltered. The amount of alkali (the baryta) is now smaller by reason of the conversion of part of it into carbonate by the carbon dioxide. The more carbon dioxide

is present, the greater will be the amount of baryta converted into barium carbonate, and the greater will be the difference between the amount of alkali originally taken and that remaining afterwards. By ascertaining the amount of oxalic acid required to neutralise a known volume of the original baryta water, and that required to neutralise the liquid which remains after partial neutralisation as already described, the quantity of carbon dioxide in the 10 litres of air may be ascertained.

**175. Other impurities in Air.**—The remaining impurities, such as suspended dust and carbon, ammonia, sulphur compounds, hydrochloric acid and chlorides, occur in much smaller and more variable quantities. During thunderstorms oxides of nitrogen are formed, and these give rise to nitrous and nitric acid; ozone is also probably produced under such circumstances. The ammonia, carbon (soot), and sulphur compounds occur in larger quantity in the vicinity of towns, from the combustion of coal, or where decaying refuse is found.

The hydrochloric acid and chlorides come for the most part from manufacturing operations, though it is significant that, especially during high wind, the air in the neighbourhood of the sea contains much more sodium chloride than is usual.

**176. The relation of Animal and Plant Life to Air.**—By breathing on a cool glass surface, and by expelling air from the lungs through lime-water, it is easy to demonstrate that expired air contains large quantities of moisture and carbon dioxide. Indeed the expired air from man contains usually over 4 per cent of carbon dioxide, that is, over one hundred times as much as normal air.

The agencies at work in producing carbon dioxide are—

(1) Respiration of animals and plants; (2) Combustion of fuel; (3) Decay of organic matter, (4) Subterranean causes.

Faraday calculated that nearly five million tons of carbon dioxide were contributed daily to the atmosphere by these processes. Under such a contribution the air would slowly



get more and more charged with carbon dioxide, and the percentage of oxygen would diminish.

There are, however, processes constantly in operation which act in the opposite direction.

(1) In the process of assimilation in plants, the green colouring matter (chlorophyll), in presence of direct or diffused sunlight, effects the decomposition of carbon dioxide and liberates oxygen.

(2) Carbon dioxide being moderately soluble in water is carried down by rain, and is also taken up by surface waters and sea water

The precise extent to which the loss and gain counteract one another is difficult to estimate, but that plant life is an important factor is shown by actual observations on the living plant, and by the variations in the amount of carbon dioxide in air in the neighbourhood of forests in the daytime, when the foliage is exposed to the sun's rays, as compared with night, when assimilation is checked and only respiration goes on

**177. Is Air a compound or a mixture of Nitrogen and Oxygen?**—We have seen that a chemical compound shows the following characters:—

(1) It possesses a *definite* composition (see § 46).

(2) The weights of the elements composing it are in proportion to the atomic weights, or in some simple multiple proportion of the atomic weights. This follows from the Atomic Theory—see Chap. VII.

(3) The compound shows distinctive physical and chemical properties, the individual properties of the constituent elements being more or less completely concealed (see § 45).

(4) When combination takes place, heat is usually evolved

(5) When gases combine to form a gaseous compound there is generally a contraction in volume, thus—

2 vols. of hydrogen + 1 vol. of oxygen form 2 vols. of  
water vapour.

3 vols. of hydrogen + 1 vol. of nitrogen form 2 vols. of  
ammonia.

(6) The simple solution of a gas in water does not affect its chemical composition; for instance, if we dissolve ammonia or carbon dioxide in water, and then, by boiling the solution, expel the gas again, it will be found to be unaltered in character or composition.

Now let us apply these tests to air.

(1) The composition of air varies very little under different circumstances, but even such small variations as are found in its composition do not occur in the case of chemical compounds.

(2) If we divide the relative proportions by weight of nitrogen and oxygen in the air by the atomic weights of nitrogen and oxygen, we shall see whether any simple multiple relation is shown. Of the 76.995 per cent. of nitrogen and argon present in air 0.937 per cent. is argon, so that the percentage of nitrogen is  $76.995 - 0.937 = 76.058$ . We have therefore—

$$\text{Nitrogen } \frac{76.058}{14} = 5.433;$$

$$\text{Oxygen } \frac{23.005}{15.96} = 1.441;$$

$$\text{And } 5.433 : 1.441 :: 3.77 : 1.$$

That is, to be even approximately in agreement with the results of analysis we should have to assume a compound  $\text{N}_{15}\text{O}_4$  ( $3.77 : 1 = 15.08 : 4$ ). The same result may be arrived at by considering the volume relations of nitrogen and oxygen in air.

(3), (4), and (5) Nitrogen and oxygen retain their characters with slight modification in air, and a mixture of the two gases in the proper proportions shows precisely the same characters in all respects as air. No heat is evolved when they are brought together, nor does any contraction in volume take place.

(6) We have seen (§ 109) that when air is shaken up with water, a greater proportion of oxygen dissolves than nitrogen, owing to the greater degree of solubility of oxygen, so that whilst in the air originally taken, one volume of oxygen is associated with approximately four

volumes of nitrogen, air dissolved in water consists of one volume of oxygen associated with two volumes of nitrogen.

On all these grounds, therefore, we must admit that air is simply a *mixture* of nitrogen and oxygen.

The following additional reasons may be mentioned:—

(7) The constituents of air can be partly separated by diffusion, for, owing to the difference in density of nitrogen and oxygen, they do not diffuse through a porous membrane at equal rates (see § 55); if the gases were combined the compound would diffuse *as a whole*.

(8) When liquid air boils the nitrogen distils off before the oxygen and argon.

(9) The refractive index of air is the mean of those of oxygen and nitrogen; in the case of compounds the value is invariably found to be either above or below the mean of the values for the constituents.

178. Fogs are caused by condensation of water vapour induced by dust. That dust is the cause of fog formation is proved by the fact that in filtered air fogs cannot form. Analysis of the deposit left after a fog showed it to consist of carbon, hydrocarbons, sulphuric acid, iron and its oxides, and silica. During a fog, too, the amount of carbon dioxide increases enormously and reaches from three to five times the normal amount.

#### ARGON AND ITS COMPANIONS.

179. In the year 1894 Lord Rayleigh noticed that the density of nitrogen obtained from the air was about 0.4 per cent greater than that of nitrogen prepared by chemical methods. The only explanation which could be offered was that air contained a small quantity of another inert gas in addition to nitrogen, and that this gas had a greater density than nitrogen. Ramsay took up the question and succeeded in isolating this gas; he passed air freed from carbon dioxide and water vapour over red-hot copper which removed the oxygen, and then over red-hot

magnesium which removed the nitrogen. The residue amounted to about 1 per cent. of the air used, and consisted of a very inert gas which Ramsay could not decompose or cause to combine with any known substance. He came to the conclusion that the new gas was an *element*, and on account of its inertness he called it *argon*. Argon has a molecular weight of 40 as determined from its density, and its molecule has been shown to contain one atom, the atomic weight is therefore also 40. Argon liquefies at  $-187^{\circ}\text{C}$  and solidifies at  $-189.5^{\circ}\text{C}$ .

More recently Ramsay has discovered several other new elementary gases in the atmosphere, namely, *helium*, *neon*, *krypton* and *xenon*. He fractionally distilled large quantities of liquid air, and from the lowest boiling portions isolated two elements, helium and neon. From the portions boiling at a higher temperature than oxygen, nitrogen and argon, he isolated krypton and xenon. These elements are only present in exceedingly small quantities in the atmosphere, they are all very inert like argon and have not, up to the present, been induced to combine with any known substance.

As in the case of argon, so with these other elements the molecule contains one atom.

**Helium** has been found in some uranium ores and in certain springs as well as in the atmosphere. Helium is the most difficult of all gases to liquefy, its boiling-point being very near the absolute zero of temperature. Its atomic weight is 4.

The atomic weights of neon, krypton and xenon are respectively 20, 81.75 and 128.

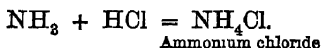
### AMMONIA, $\text{NH}_3$ .

**180. Occurrence.**—Ammonia or its compounds exist in small quantities in air and in natural waters, being produced either from the nitrogen present in the air, or by the action of bacteria from refuse matters in the soil.

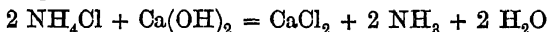
\* It has recently been found better to mix the magnesium with quicklime

**181. Preparation.**—Whenever animal or vegetable products containing nitrogen are strongly heated in closed retorts (air being excluded), and especially when they are heated with lime or other alkalies, ammonia is given off.

In this way large quantities of ammonia are obtained during the distillation of coal (which contains about  $1\frac{1}{2}$  per cent. of nitrogen), the coal gas being cooled and then washed, by which means any ammonia is separated and obtained in solution. The further distillation of the liquid so obtained with lime sets free the ammonia, which, if passed into aqueous hydrochloric acid, forms ammonium chloride or sal ammoniac—



In the laboratory ammonia is usually prepared by heating a mixture of ammonium chloride and slaked lime,  $\text{Ca}(\text{OH})_2$ —



**Exp. 127** —Weigh out about 10 grammes of ammonium chloride and 20 grammes of dry slaked lime and grind them up in a mortar till they are in a state of a fine powder and intimately mixed. Introduce the mixture into a small dry round-bottomed flask, and connect this with a U-tube containing lumps of quicklime or caustic soda, as shown in Fig. 48. Now heat the flask gently when ammonia will be evolved, and after being dried by the lime or caustic soda in the U-tube may be collected by upward displacement, being much lighter than air. Ammonia can also be collected over mercury, but not over water in which it is very soluble.

The ordinary drying agents for gases—sulphuric acid, calcium chloride and phosphorus pentoxide—cannot be used in the case of ammonia, since it combines readily with them.

**182. Properties.**—Ammonia is a colourless gas, having a very pungent but not disagreeable odour if diluted with much air; in the pure condition it is injurious when breathed in quantity. At  $-34^\circ \text{C}$ . under ordinary pressure, and at  $0^\circ \text{C}$  under a pressure of seven atmospheres, dry ammonia condenses to the liquid form (see below, Carré's apparatus).

**Exp 128.**—Fill a litre flask by displacement with dry ammonia, and show its solubility in the same way as already described (Exp 118)

Water at  $0^{\circ}\text{C}$ . dissolves 1,050 times its volume of the gas, and at  $15^{\circ}\text{C}$ . 727 volumes. The aqueous solution is lighter than water, and in its most concentrated form has the specific gravity 0.884; it contains 36 per cent by weight of the gas. The gas may be entirely expelled by boiling the solution.

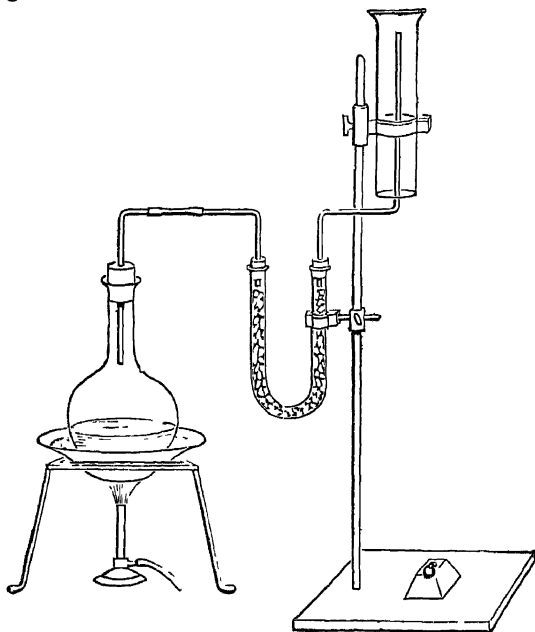


FIG 13

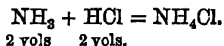
Ammonia neither burns readily in air nor supports combustion, but a mixture of warm ammonia and oxygen burns with a greenish-yellow flame.

**Exp. 129.**—Gently warm a strong solution of ammonia in a wide-mouthed eight-ounce flask, and bubble oxygen gas through the solution at the same time. A mixture of ammonia and oxygen will pass out at the open mouth of the flask, and will burn when a light is applied to it.

Metallic oxides which are reduced in hydrogen also undergo reduction when heated in ammonia gas; the hydrogen of the ammonia combines with the oxygen of the oxide to form water, and nitrogen is set free.

**183 Ammonium Salts.**—Ammonia in presence of water is a strong alkali, and combines directly with acids to form ammonium salts; this can be well shown with hydrochloric acid gas.

**Exp. 180**—Fill two similar jars by displacement with ammonia and hydrochloric acid gas respectively, and cover the mouth of each jar with a glass plate. Now bring them mouth to mouth and withdraw the glass plates. The gases as they come into contact will combine, forming a fine white powder which remains for some time diffused throughout the jars. This body is ammonium chloride,  $\text{NH}_4\text{Cl}$ —



Ammonium sulphate,  $(\text{NH}_4)_2\text{SO}_4$ , ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , and other salts may be obtained by neutralising a solution of ammonia with the respective acids, and then evaporating to dryness on a water-bath.

The ammonium salts all contain the group of atoms  $\text{NH}_4$ , which in them plays the same part as an atom of a monovalent metal.  $\text{NH}_4$  does not exist in the free state. Such a group of atoms, which enters into a series of compounds, is called a *compound radicle*. We have had an example of a compound radicle in the case of hydroxyl (OH). These two radicles combine together when ammonia gas dissolves in water, forming ammonium hydroxide,  $\text{NH}_4\text{OH}$ .

The ammonium salts strongly resemble the salts of potassium and sodium but differ from them in one important respect, namely, their behaviour towards heat. We shall study this property at some length.

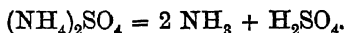
When ammonium chloride is heated, it *apparently* sublimes unchanged, the vapour condensing again to ammonium chloride. It has been shown, however, that the vapour is not that of ammonium chloride, but is a mixture

of ammonia and hydrochloric acid,\* which recombine on cooling—

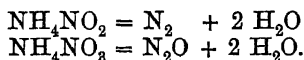


This dissociation is proved by measurement of the vapour density, and, more directly, by partially separating the two gases by diffusion.

The ammonium salts of less volatile acids, *e.g.* sulphuric and phosphoric acids, are also dissociated by heat, but in this case the volatile ammonia comes off alone, leaving the acid behind—



The ammonium salts of the oxyacids of nitrogen are not dissociated but decomposed by heat, giving either nitrogen and water, or nitrous oxide and water—



As already mentioned, ammonia combines directly with calcium chloride, the compound being represented by the formula  $\text{CaCl}_2 \cdot 8 \text{NH}_3$ .

**184. Liquefaction of Ammonia by Pressure** —If ammonia gas be generated in quantity, and the receiver into which it passes be a closed vessel much smaller than the volume of the gas generated, it will be compressed and ultimately condense by its own pressure to the liquid form. This is indeed the method of Faraday (see § 51), and a simple form of apparatus in which this principle is made use of is that of Cairé (Fig. 49). It consists essentially of a strong iron cylinder containing concentrated ammonia solution, as shown at A in the figure; this communicates with a receiver B, of relatively small volume, by means of the tube C. When A is surrounded by hot water, ammonia gas is given off freely and accumulates in the apparatus in such quantity that it condenses in the receiver B, which has been surrounded by cold water.

\* If however the ammonium chloride is *absolutely dry*, it volatilises without dissociation.



If we now reverse the arrangement and surround A with cold water, the liquid ammonia will boil very rapidly and pass back as gas into A, and this rapid transformation of liquid into gas will bring about a considerable depression of temperature in B. This vessel is provided with a space D, into which water may be introduced and frozen. By various applications of this principle, liquid ammonia is used on a large scale for obtaining low temperatures.

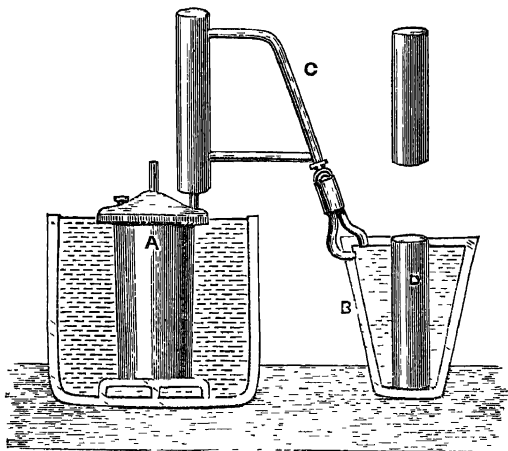
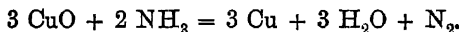


FIG. 49.

**185. Composition of Ammonia.**—The composition of ammonia may be determined by passing the gas through a red-hot tube containing copper oxide. The hydrogen is transformed into water, which may be collected and weighed in the manner already described (§ 95), and the volume of nitrogen which passes forward may also be ascertained—



The *volume* of hydrogen may be readily calculated from the weight of water obtained.

A second method depends on the fact that when electric sparks are passed through gaseous ammonia it is slowly decomposed into its constituents. Dry ammonia is passed into a eudiometer over mercury, and its volume accurately measured. The sparks are then passed until no further increase in volume occurs; the final volume will be found to be just *double* the original volume. If now excess of oxygen be passed into the eudiometer and the spark passed, the hydrogen will combine with it and form water, which condenses, leaving nitrogen and the *excess* of oxygen added, two-thirds the diminution being the volume of hydrogen. The volume of nitrogen is found by subtracting the volume of hydrogen calculated from this diminution, from the volume of nitrogen plus hydrogen obtained after the first sparking.

This method is not very accurate owing to the fact that some of the nitrogen combines with oxygen, forming oxides of nitrogen. By the electrolysis of ammonia it may however be shown that the volume of nitrogen it contains is one-third that of the hydrogen. The experiment is performed in the following manner. A saturated solution of common salt is prepared, and to this is added about one-tenth of its volume of strong ammonia. The solution is now introduced into a voltameter similar to that figured on page 193, but fitted with carbon electrodes and submitted to the action of the current from six Bunsen cells. Nitrogen collects in one tube and hydrogen in the other, and the volumes will be found to be in the proportion 1 : 3.

One of the most convenient methods of proving the volumetric composition of ammonia depends upon the fact that chlorine is capable of removing the hydrogen from it with liberation of free nitrogen, as we saw in § 168. A long glass tube closed at one end is divided into three equal parts by india-rubber bands. It is next filled with chlorine at the pneumatic trough by displacement of chlorine water, and when quite full the mouth is closed by a cork carrying a small dropping funnel, this is done *before* the tube is removed from the trough so as to prevent any chlorine escaping. The tube is now placed in an upright

position and about 10 cubic centimetres of strong ammonia solution are introduced into the funnel. This solution is allowed to flow into the tube drop by drop: the first drop which enters reacts with the chlorine with formation of a yellowish-green flame, and as more ammonia enters dense clouds of ammonium chloride are produced. When all the ammonia has been run in, a little dilute hydrochloric acid is introduced through the funnel to combine with the excess of ammonia. The gas which now remains in the tube is nitrogen under reduced pressure. In order to bring it to atmospheric pressure the funnel is filled with dilute hydrochloric acid; a tube bent twice at right angles, with one long arm and one short arm, is also filled with dilute acid, and the short arm is attached to the funnel by rubber tubing, whilst the long arm is dipped into some more acid contained in a beaker (see Fig 50). On now opening the tap hydrochloric acid is sucked into the tube until the pressure is the same as that of the atmosphere. It will then be found that the liquid reaches to the second india-rubber band, *i. e.* the nitrogen occupies one-third of the tube. Now hydrogen and chlorine unite in equal volumes to form hydrochloric acid, so that the volume of hydrogen extracted from ammonia by the chlorine in the tube would just fill the tube. This hydrogen was originally in combination with the nitrogen left in the tube, so that the relative volumes of hydrogen and nitrogen in ammonia are in the ratio 1 : 3.

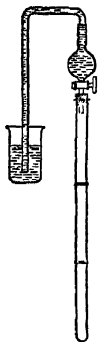


FIG 50

By combining with this result a knowledge of the density of ammonia we can completely prove its composition.

Since the volumes of nitrogen and hydrogen which combine to form ammonia are in the ratio 1 : 3, it follows by Avogadro's hypothesis that the number of molecules of nitrogen and hydrogen which combine are in the same ratio. But the molecules of these two elements each contain two atoms, and therefore—

$$\frac{\text{Number of atoms of nitrogen in ammonia}}{\text{Number of atoms of hydrogen in ammonia}} = \frac{1}{3}$$

The formula of ammonia is, therefore,  $\text{NH}_3$  or  $\text{N}_2\text{H}_6$  or  $\text{N}_3\text{H}_9$ , etc.

Now the relative density of ammonia is 8.5 ( $\text{H} = 1$ ), and consequently its molecular weight is  $8.5 \times 2 = 17$ .

Let us take first the simplest formula, viz.  $\text{NH}_3$ . Since atomic weight of  $\text{N} = 14$  and atomic weight of  $\text{H} = 1$  the molecular weight of  $\text{NH}_3$  is  $14 + 1 \times 3 = 17$ . This agrees with the number obtained from the density, so that  $\text{NH}_3$  is the correct formula.

**186. Tests for Ammonia.**—Ammonia may be recognised by its smell, action on litmus, and by giving dense white fumes of ammonium chloride when brought in contact with hydrochloric acid gas. With Nessler's solution ammonia gives a characteristic brownish coloration or precipitate, according to the amount of ammonia present.

All ammonium compounds give off ammonia when treated with lime or caustic potash.

## QUESTIONS.—CHAPTER XVI.

1. Describe a method by which nitrogen may be obtained from air by removal of oxygen.
2. Give two methods for the preparation of nitrogen from ammonia or ammonium salts.
3. State the chief physical and chemical properties of nitrogen.
4. Describe a method of determining the composition of the atmosphere by volume.
5. How may the composition of the air by weight be determined?
6. A mixture of 25 c.c. of air and 50 c.c. of hydrogen is exploded in a eudiometer, and the volume of the residual gas is found to be 60.3 c.c.; find the percentage of oxygen in the air.
7. The percentage composition of air by weight being

76.058 nitrogen, 0.937 argon and 23.005 oxygen, find the composition by volume.

8. A litre of dry air is passed over heated copper and the increase in the weight of the copper found to be 0.297 gramme: find the percentage by weight of oxygen in the air. (1 litre of air weighs 1.293 gramme.)
9. How would you show that air contains carbon dioxide, and what means would you adopt for ascertaining the amount of carbon dioxide in air?
10. How do the following impurities originate in air:—carbon dioxide, sodium chloride, ammonia, sulphurous acid?
11. What agencies are at work which tend to remove such impurities as carbon dioxide and ammonia from the air?
12. In what respect does a *mixture* of two gases, such as nitrogen and oxygen, differ in its behaviour from a *compound* of the two gases when shaken up in contact with water?
13. What indications are usually shown that two gases which you have brought together have entered into combination?
14. What reasons are there for supposing that the nitrogen and oxygen in air are mixed, not chemically combined?
15. Write a short account of argon and the other elements recently discovered in the atmosphere.
16. Give a general method by which ammonia may be obtained from nitrogenous animal or vegetable substances.
17. How would you prepare and collect dry ammonia?
18. How can it be shown that ammonia contains hydrogen?
19. Explain what is meant by a *compound radical*.
20. What experiments would you make to show that the composition of ammonia is rightly expressed by the formula  $\text{NH}_3$ ?
21. Under what circumstances do nitrogen and hydrogen enter into combination, and under what circumstances is the compound so formed decomposed again without the intervention of chemical reagents?

## CHAPTER XVII.

### OXIDES AND OXYACIDS OF NITROGEN.

187. IN the following table is given a list of the oxides and oxyacids of nitrogen :—

Nitrous oxide, $N_2O$ .	Hyponitrous acid, $H_2N_2O_2$
Nitric oxide, $NO$ .	
Nitrogen trioxide or nitrous anhydride, $N_2O_3$ .	Nitrous acid, $HNO_2$ .
Nitrogen peroxide, $N_2O_4$ .	
Nitrogen pentoxide or nitric anhydride, $N_2O_5$ .	Nitric acid, $HNO_3$ .

**Occurrence.**—The higher oxides are formed in small quantity when the electric discharge takes place in a mixture of nitrogen and oxygen. These oxides, or nitrous and nitric acid formed from them, therefore occur in the atmosphere and in rain water; waters contaminated by the drainage of surface soil, or by decaying nitrogenous organic matter, also contain similar products. In all such cases, owing to the difficulty of bringing about direct combination of nitrogen and oxygen, they are present in very minute quantities. Nitric acid or the nitrates being in all cases the source from which the oxides of nitrogen are derived, we shall treat these first.

NITRIC ACID,  $\text{HNO}_3$ 

**188. Preparation.**—Nitric acid, being a volatile acid, is expelled from nitrates by the action of less volatile acids, such as concentrated sulphuric acid (or silica), and this reaction is made use of in its preparation, nitrate of potash or soda being usually employed.

**Exp. 131.**—Introduce 20 grammes of potassium nitrate into a stoppered retort, and as much concentrated sulphuric acid as will just cover it. Apply a moderate heat, and presently the vapour of nitric acid will pass over and condense in the neck of the retort. The liquid may be collected in a small flask slipped over the mouth of the retort, and kept cool by means of a stream of cold water or a wet cloth. When about 10 c.c. have been distilled over, or so soon as whitish fumes of sulphuric acid begin to appear, the experiment should be stopped—



**189. Properties of the Acid.**—The pure acid is a colourless, fuming liquid, of specific gravity 1.53, boiling at  $86^\circ \text{C}$ . with partial decomposition into nitrogen peroxide, oxygen and water. It is highly corrosive, and by contact instantly stains the skin yellow, more prolonged exposure giving rise to serious wounds. Dry straw and woody fibre are charred or even set fire to by contact with it. It mixes with water in all proportions, and if the dilute solution be concentrated in air at atmospheric pressure it becomes stronger until 68 per cent. of acid is present; it then distils unchanged at  $120.5^\circ \text{C}$ . under normal pressure. Similarly, on distilling an acid stronger than this, it gradually becomes weaker till it contains 68 per cent of  $\text{HNO}_3$ , when it passes over unchanged. If the pressure is not normal the composition and boiling-point of the acid which distils unchanged have different values, as in the case of the halogen acids.

As already stated, pure nitric acid decomposes to some extent at its boiling-point; at higher temperatures this decomposition takes place very readily, as may be illustrated by the following experiment:—

**Exp. 132.**—Support a clay pipe in the position shown in the diagram by means of a retort-stand and clamp (not shown). Heat the tube strongly at a spot about 9 inches from the bowl by means of a Bunsen burner, and then pour about 5 c.c. of strong nitric acid into the bowl. On reaching the heated part, decomposition takes place, and the weight of acid above pushes

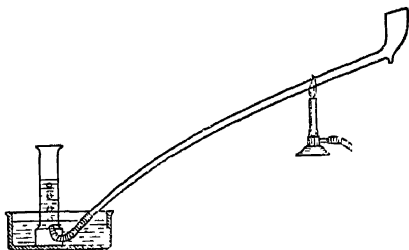
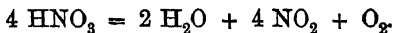


FIG 51.

the gaseous products out through the stem of the pipe. The oxygen may be collected over water; the nitrogen peroxide being soluble goes into solution.

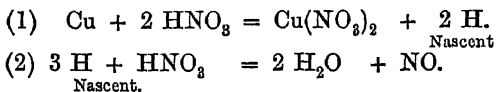
The equation representing the decomposition of nitric acid on heating is—



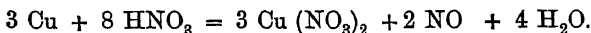
On account of the large percentage of oxygen which nitric acid contains (76 per cent.), and of the ease with which it parts with some of this oxygen, we should expect it to possess strong oxidising properties, and such is the case. Thus it readily transforms C, S, P and I into  $\text{CO}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$  and  $\text{HIO}_3$  respectively, whilst turpentine when mixed with it inflames.

**190. Action on Metals**—Most metals dissolve readily in nitric acid with evolution of red fumes, the nitrate of the metal, or in some cases the oxide, being formed. It is only rarely that free hydrogen is one of the products of the reaction. We may suppose that the first action of nitric acid on a metal is to convert it into the nitrate with liberation of *nascent* hydrogen, but the latter is immediately oxidised to water by a further quantity of nitric acid. Thus, taking the case of copper which reduces dilute nitric acid chiefly to nitric oxide, the two stages may be thus represented—

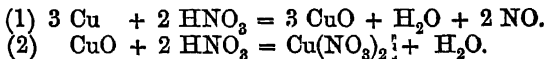




On combining the two equations we get for the whole reaction—



The reaction may, however, be explained in another way, namely, by supposing that nitric acid first converts the metal into an oxide itself undergoing reduction, and then the oxide reacts with a further quantity of nitric acid, producing a nitrate of the metal and water—



It is beyond the scope of this book to discuss the relative merits of these two explanations.

The products of the reduction of nitric acid by metals may consist of any of the following substances: nitrogen peroxide, nitrous acid, nitric oxide, nitrous oxide, nitrogen and ammonia.

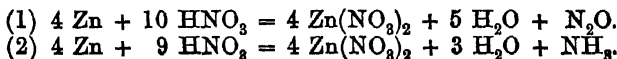
The exact course of the reaction depends upon the following factors:—

- (1) The nature of the metal.
- (2) The strength of the acid.
- (3) The temperature.
- (4) The concentration of the products in solution.

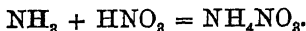
Thus we have seen that with moderately dilute acid copper forms chiefly nitric oxide; with strong nitric acid, however, the main product is nitrogen peroxide—



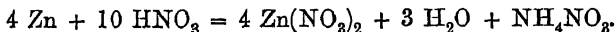
Again, zinc with dilute nitric acid yields chiefly nitrous oxide, but with a somewhat stronger acid a large proportion of ammonia results—



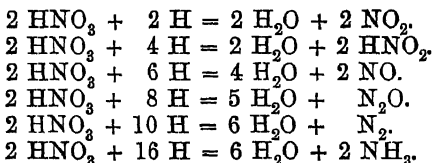
The ammonia produced combines with the excess of nitric acid to produce ammonium nitrate—



So that equation (2) is more correctly expressed—

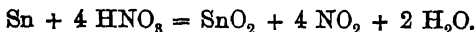


The relative amount of reduction which nitric acid has undergone when the products nitrogen peroxide, nitrous acid, etc., are formed, can be well illustrated in the following manner, regarding nascent hydrogen as the reducing agent:—



It will be noticed that the number of atoms of hydrogen required to reduce two molecules of nitric acid successively increases from nitrogen peroxide to ammonia.

The metals which *do* liberate free hydrogen from nitric acid are *magnesium* and *manganese*, the main products with the dilute acid being in both cases ammonia and hydrogen. When a metal such as mercury is capable of forming two nitrates the lower one is produced when the metal is in excess, the higher when the acid is in excess. Tin with quite dilute acid gives stannous nitrate, but with stronger acid it behaves in an unusual manner, being converted into stannic oxide,  $\text{SnO}_2$ —



Antimony is similarly oxidised to antimony pentoxide,  $\text{Sb}_2\text{O}_5$ .

191. **The passive state.**—Pure concentrated nitric acid does not attack iron, nickel or tin.

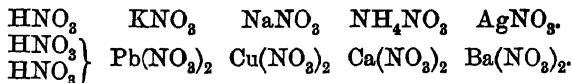
It was formerly supposed that the acid covered them with a coating of a higher oxide of the metal, which prevented the further action of the acid, rendering the metals "passive." Recently it has been suggested that the cause of the phenomenon is an electrical one, but the true explanation is still a matter of doubt.

192. **Aqua Regia**—The so-called "noble" metals, such as gold and platinum, are not acted upon by nitric acid of any strength, but readily dissolve in a mixture of hydrochloric and nitric acids\* which has for this reason been termed *aqua regia*.

The cause of the difference is that hydrochloric and nitric acids mutually interact setting free chlorine, which, especially in the nascent state, readily attacks gold and platinum—



193. **The Nitrates.**—These salts may be looked upon as nitric acid in which the hydrogen of the acid is replaced by a metal, thus—



They may be produced by the action of the acid on the metals or on their oxides, hydroxides, or carbonates.

**Exp. 133.**—To a few cubic centimetres of *dilute* nitric acid contained in a porcelain basin add fragments of lead, and digest on a water-bath until the acid is saturated and no more of the metal will dissolve. Evaporate the clear liquid to dryness, when a white salt, nitrate of lead, remains.

**Exp. 134**—Dilute 5 c. c. of nitric acid with an equal bulk of water, and add a little litmus solution, which will become of a bright red colour. Now add ammonia solution little by little until the last

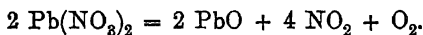
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\* *Aqua regia* is usually made by mixing nitric acid with four times its volume of hydrochloric acid.

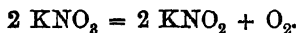
drop turns the litmus blue, and concentrate the liquid to a point at which, when a drop of it is allowed to cool on the end of a glass rod, it crystallises. On standing, crystals of ammonium nitrate will be obtained.

All the nitrates are soluble in water: those of the alkali metals are the most stable, and those of the heavy metals the least stable. When strongly heated all undergo decomposition.

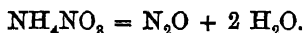
Nitrates of the heavy metals evolve oxides of nitrogen (generally  $\text{NO}_2$ ) and oxygen, leaving an oxide of the metal—



Nitrates of the alkali metals (K, Na) evolve oxygen, leaving a nitrite—



Ammonium nitrate decomposes in an exceptional way, forming nitrous oxide and water—



Nitrates when heated naturally exert a powerful oxidising action on substances which may be mixed with them.

**Exp. 135.**—Heat a few grammes of potassium nitrate in a test-tube until it fuses, and then drop into it one or two fragments of dry charcoal. The charcoal will ignite and burn with violence, being oxidised by the nitrate to  $\text{CO}_2$ .

**Exp. 136** —Repeat the experiment, introducing a few small shavings of lead; the lead will be oxidised at the expense of the nitrate and transformed into a yellowish powder, oxide of lead.

**194. Tests for Nitrates.**—(1) Nitrates when heated with sulphuric acid or silica give off nitric acid fumes, often accompanied by red fumes of nitrogen peroxide.

(2) Mix a solution of a nitrate with strong sulphuric acid, and add copper turnings; on warming red fumes will be given off.

(3) (The most sensitive test). Mix a cold solution of a nitrate with a cold strong solution of ferrous sulphate, and pour gently down the side of the tube strong sulphuric acid: the latter sinks to the bottom, and a dark ring forms

above it. The sulphuric acid liberates nitric acid from the nitrate, and the ferrous sulphate reduces the nitric acid to nitric oxide, which combines with more ferrous sulphate to form the dark-coloured solution.

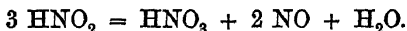
195. **Uses of Nitric Acid.**—Nitric acid is largely used in the manufacture of a number of important substances such as sulphuric acid, nitroglycerine, guncotton, colours, and nitrates. Among the last may be mentioned silver nitrate, which is used in photography, strontium and barium nitrates, which are used in pyrotechny, and lead nitrate which is employed in calico-printing. Nitric acid is also used in Grove's and Bunsen's electric batteries.

#### NITROUS ACID, $\text{HNO}_2$ .

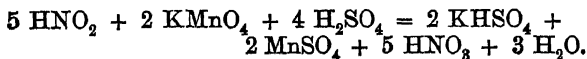
196. This acid is only known in dilute aqueous solution. It may be prepared by adding a strong acid such as hydrochloric acid to a solution of a nitrite, *e.g.* potassium nitrite,  $\text{KNO}_2$ —



The aqueous solution gradually decomposes at ordinary temperature, and more rapidly on warming, according to the equation—

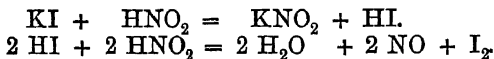


Nitrous acid is capable of acting both as a reducing agent and as an oxidising agent; as the former towards substances which readily give up oxygen, and as the latter towards those which readily take up oxygen. Thus it is rapidly converted into nitric acid by potassium permanganate, the latter being reduced and decolorised. In the presence of dilute sulphuric acid the reaction which takes place may be thus represented—



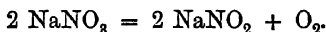
On the other hand, nitrous acid liberates free iodine from

potassium iodide. We may suppose that free hydriodic acid is first formed by double decomposition, and that this is then oxidised by the excess of nitrous acid—

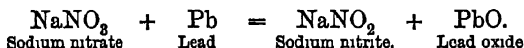


197. Nitrites.—The nitrites of the alkali metals may be formed—

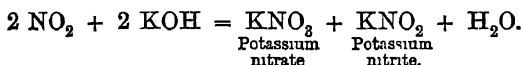
(1) By heating the corresponding nitrates, *e. g.*—



If the nitrate is heated with certain metals, such as lead, the decomposition is brought about more readily, the metal taking up the oxygen—



(2) By the action of nitrogen peroxide on the caustic alkalis. In this case nitrates are formed simultaneously—



All nitrites are soluble in water, but silver nitrite,  $\text{AgNO}_2$ , is only sparingly soluble, and is formed as a white precipitate when a strong solution of silver nitrate is mixed with a strong solution of sodium nitrite.

198. Tests for Nitrites.—(1) The evolution of red fumes (nitrogen peroxide) when the salt is treated with sulphuric acid.

(2) The formation of a dark ring at the surface of contact when a solution of ferrous sulphate is poured upon a solution of a nitrite, to which *dilute* sulphuric acid has been added (in some cases the addition of acid is unnecessary).

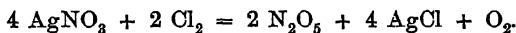
(3) The liberation of iodine from potassium iodide on the addition of an acid, *e. g.* sulphuric acid, and the decolorisation of potassium permanganate solution in presence of acetic acid.

NITROGEN PENTOXIDE,  $N_2O_5$ .

199. This is a white crystalline solid obtained by the action of a powerful dehydrating agent, such as phosphorus pentoxide, on nitric acid. The acid is introduced into a retort and well cooled by means of a freezing mixture. A quantity of phosphorus pentoxide equivalent to the acid used is gradually added, and on now gently warming the mixture nitrogen pentoxide distils over and is collected in a cooled receiver—



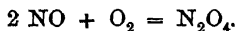
A second method of preparation is to pass dry chlorine over dry silver nitrate—



Nitrogen pentoxide enters into combination with water with great energy, reproducing nitric acid; it is therefore the anhydride of this acid. It is an unstable body and undergoes decomposition with explosive violence when heated.

NITROGEN TETROXIDE OR PEROXIDE,  $N_2O_4$  or  $\text{NO}_2$ .

200. Preparation.—Nitrogen peroxide is formed on the direct combination of nitric oxide,  $\text{NO}$ , with oxygen—

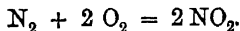


It may also be prepared by heating lead nitrate—



**Exp. 137.**—Introduce 10 grammes of finely-powdered lead nitrate into a retort of "hard" glass (see Fig. 52) connected with a U-tube surrounded by a freezing mixture (pounded ice or snow and salt) and heat strongly. Red fumes are given off and condense in the U-tube to a colourless liquid,  $\text{N}_2\text{O}_4$ . Remove the freezing mixture and note that as the temperature rises the liquid darkens in colour, and at ordinary temperatures is *orange yellow*.

Nitrogen peroxide is also formed to some extent when electric sparks are passed through a mixture of nitrogen and oxygen—



201. **Properties.**—The liquid obtained as in the experiment just described passes, on strongly cooling, into a colourless solid, melting at  $-10^\circ \text{C}$ . If, on the other hand, its temperature is further raised it continues to get darker, and at  $22^\circ \text{C}$ . boils, giving off a reddish-brown vapour; the

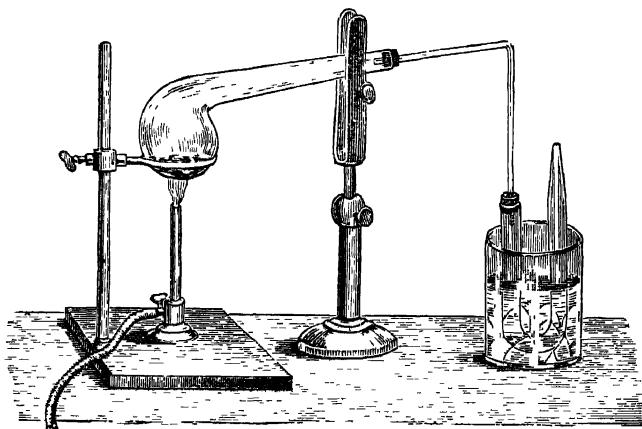


FIG. 52.

vapour, in its turn, continues to darken with rise of temperature till it becomes almost black. This change in colour is accompanied by a corresponding change in composition. Thus at low temperatures ( $-10^\circ \text{C}$ .) nitrogen peroxide has the composition  $\text{N}_2\text{O}_4$ , and at  $140^\circ$  it has completely dissociated into  $\text{NO}_2$  molecules, whilst at intermediate temperatures some of the molecules are  $\text{N}_2\text{O}_4$ , others are  $\text{NO}_2$ . That this is the true explanation is proved by the changes in density which the gas undergoes with rise of temperature.

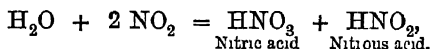


In the following table the values of the relative density ( $H = 1$ ) are given for several different temperatures, and also the corresponding molecular weights.

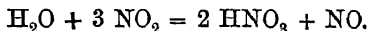
Temperature	Relative density.	Molecular weight.
26·7°	38 3	76 6
60 2°	30 1	60 2
100·1°	24 3	48·6
135·0°	23 1	46·2
140·0°	23 0	46 0

Now the molecular weight of  $N_2O_4$  is 92, and that of  $NO_2$  is 46, from which it follows that at 140° C. the dissociation into  $NO_2$  molecules is complete, but at 26·7° C the greater part of the gas consists of  $N_2O_4$  molecules. By means of the lowering of freezing-point method of determining molecular weights, it has further been shown that at low temperatures nitrogen peroxide is composed of  $N_2O_4$  molecules.

Nitrogen peroxide is not a supporter of combustion in the ordinary sense, *i.e.* it extinguishes a lighted taper, but substances which burn in oxygen and give out sufficient heat to decompose the nitrogen peroxide will also burn in the latter. Thus brightly burning phosphorus continues to burn in the gas with a dazzling light. Nitrogen peroxide is decomposed by water, the exact course of the reaction depending on the conditions. Thus with a small quantity of cold water, nitric and nitrous acids are produced—



but with hot water the reaction proceeds thus—



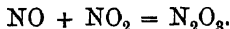
This is what we might expect when we remember the ease with which nitrous acid decomposes into nitric acid and nitric oxide. During the solution of nitrogen peroxide in water the liquid passes through a series of colour changes—blue, green and orange. This is supposed to be

due to the gradual solution of the nitrogen peroxide in the nitric acid formed. Of course, in the presence of sufficient water all the nitrogen peroxide is decomposed and the solution becomes colourless.

The gas attacks many metals, such as mercury, copper and iron. It is very poisonous.

### NITROGEN TRIOXIDE, $N_2O_3$ .

202. This oxide is obtained as a deep-blue liquid by passing nitric oxide into nitrogen peroxide, the temperature not being allowed to rise above  $-21^\circ \text{C}$ .

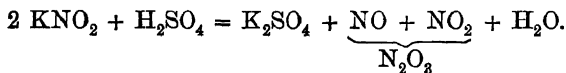


Nitrogen trioxide is very unstable, and even at  $-20^\circ \text{C}$ . commences to decompose into nitrogen peroxide and nitric oxide—

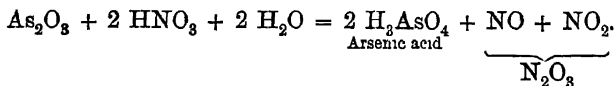


It cannot exist in the gaseous state.

We saw in § 196 that nitrous acid is produced by the action of a strong acid on a nitrite. At the same time, however, brown fumes are evolved, consisting of a gas which corresponds in percentage composition to nitrogen trioxide (*i. e.* the anhydride of nitrous acid) but really consists of a mixture of nitric oxide and nitrogen peroxide—



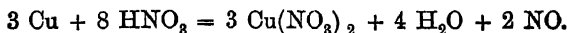
The same mixture of oxides is obtained by the action of nitric acid on arsenious oxide,  $\text{As}_2\text{O}_3$ —



If the brown fumes obtained by either of these processes are cooled down to  $-21^\circ \text{C}$ . combination takes place with formation of nitrogen trioxide.

## NITRIC OXIDE, NO.

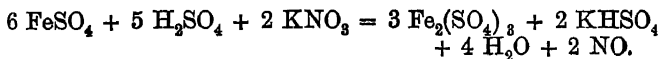
• 203. **Preparation.**—Nitric oxide is usually prepared by the action of moderately dilute nitric acid on copper. The reaction, which we have already discussed under Nitric Acid, is—



**Exp 138**—Introduce a few grammes of copper turnings into an 8-ounce flask provided with a thistle funnel and delivery tube, and add about 50 c.c. of a mixture of equal parts of nitric acid and water. In a few moments gas begins to be evolved without the application of heat, and red fumes appear in the flask.

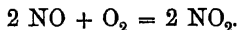
These red fumes are formed by the action of the nitric oxide on the oxygen contained in the flask; after a time the colour disappears as they are displaced, and the gas may then be collected over water at the pneumatic trough.

The gas so produced is not pure; it may contain other reduction products of nitric acid, such as nitrous oxide. The best method of preparing pure nitric oxide is to warm a solution of ferrous sulphate and potassium nitrate, acidified with dilute sulphuric acid—



204. **Properties**—Nitric oxide is a colourless gas not very soluble in water, which dissolves about  $\frac{1}{20}$ th of its volume of the gas under ordinary conditions. It is very difficult to liquefy, requiring a pressure of 104 atmospheres at  $-11^\circ \text{ C.}$ ; the liquid boils under normal pressure at  $-93^\circ \text{ C.}$

Nitric oxide by mere admixture with oxygen combines with it, as we have seen, giving rise to red fumes of nitrogen peroxide—



**Exp. 139.**—Expose a jar of the gas to air, and observe the red fumes.

**Exp 140.**—Pass oxygen little by little into a jar of the gas standing over water, allowing an interval to elapse between each addition. Red fumes will be formed, and these will dissolve in the water, which gradually rises in the jar. If the gas is pure and the oxygen be added in the proper proportion, the water will rise so as to completely fill the jar. A dilute solution of nitrous acid is thus formed, and may be shown to liberate iodine from potassium iodide, or to decolourise permanganate of potash.

Nitric oxide is the most stable of the oxides of nitrogen, and is only decomposed at a red heat ( $600^{\circ}\text{C}.$ ) It does not support combustion except when sufficient heat is evolved to decompose it, the oxygen which is liberated being the actual supporter of the combustion. Thus a lighted taper, burning sulphur and feebly burning phosphorus are extinguished by it, but fully ignited phosphorus continues to burn brightly.

**Exp 141.**—Try whether a lighted taper, burning sulphur and phosphorus when just lighted, will continue to burn in the gas, then try phosphorus which has become fully ignited.

Nitric oxide dissolves readily in a solution of ferrous sulphate, forming a brown compound  $(\text{FeSO}_4)_2 \cdot \text{NO}$ . This is the compound forming the "brown ring" in the test for nitrates. On gently warming, this compound dissociates into ferrous sulphate and nitric oxide which is evolved in a pure state.

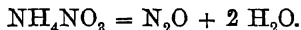
**205. Composition of Nitric Oxide**—When iron is heated in nitric oxide it combines with the oxygen and sets free the nitrogen. The gas first expands by the heat, and the iron then burns forming tri-ferrous tetroxide,  $\text{Fe}_3\text{O}_4$ . On the completion of the reaction only nitrogen remains, and this gas will be found to occupy half the volume of the original gas. Hence one molecule of nitric oxide contains one atom of nitrogen, and its formula may be expressed  $\text{N}_1\text{O}_x$ . To determine the value of  $x$  we must ascertain the density of nitric oxide compared with hydrogen. It will be found to be 15, and since the hydrogen molecule,  $\text{H}_2$ , weighs 2, the molecule of nitric oxide must weigh  $15 \times 2 = 30$ , *i. e.*

$N_1O_x = 30$ . But  $N_1 = 14$ ; therefore  $O_x = 30 - 14 = 16$ . Now the atomic weight of oxygen is 16, and therefore  $x = 1$ , *i. e.* the molecule of nitric oxide is represented by  $NO$ .

### NITROUS OXIDE, $N_2O$ .

206. This gas is familiarly known as "laughing gas," because when breathed in small quantity it produces a feeling of exhilaration. Inhaled in larger quantities it is an anæsthetic, and renders the subject insensible to pain. It is for this reason employed in dentistry.

**Preparation.**—It has already been pointed out (§ 190) that when nitric acid (dilute) is acted upon by zinc, nitrous oxide is formed. It is more usual, however, to prepare it by heating ammonium nitrate, the decomposition being represented by the equation—



**Exp 142**—Introduce about 30 grammes of dry ammonium nitrate into a 4-ounce flask and heat gently—just so as to bring about a steady and not too rapid evolution of the gas. The delivery tube should be wider than usual, as the salt is liable to be carried over and to stop up the tube; also stop the experiment when about two-thirds of the salt has been decomposed or an explosion may ensue. Cold water dissolves about its own volume of the gas; it may, however, be collected over hot water.

207. **Properties of Nitrous Oxide.**—It is a colourless gas with an agreeable odour and taste. It condenses at  $15^\circ C$ . under a pressure of 40 atmospheres to a liquid which boils at  $-92^\circ C$ . under ordinary pressure. One hundred volumes of water dissolve 130 volumes of the gas at  $0^\circ C$ ., 92 at  $10^\circ C$ ., and 67 at  $20^\circ C$ .

It is easily decomposed by heat, and supports combustion almost as readily as oxygen.

**Exp 143.**—Plunge a glowing taper into a jar of nitrous oxide, and it will burst into flame just as it does in oxygen. Sulphur and phosphorus also burn in the gas with almost as much vigour as in oxygen, though if only feebly ignited they may be extinguished. To distinguish it from oxygen, pass nitric oxide into the gas, no red fumes will appear.

**208 Composition of Nitrous Oxide** —The composition of the gas may be determined by the combustion of potassium in it and by an estimation of the density. The combustion experiment may be carried out in the apparatus shown in

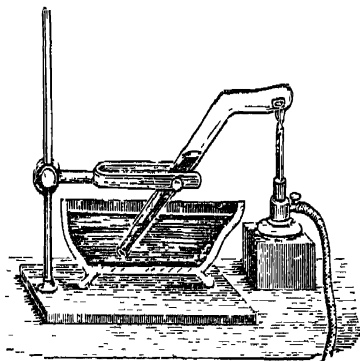
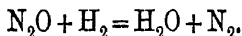


FIG 53.

Fig. 53, the gas being confined over mercury. It will be found that when the residual gas has cooled down to the ordinary temperature there is no change in volume, showing that nitrous oxide contains its own volume of nitrogen.

The formula must therefore be  $N_2O_x$ . But the density is 22, corresponding to a molecular weight 44; therefore the weight of oxygen in a molecule of nitrous oxide is  $44 - 2 \times 14 = 16$ . It follows that  $x=1$ , and the formula is  $N_2O$ .

The composition may also be determined by exploding with excess of hydrogen in a eudiometer, when the reaction is—



The residual gas consists of nitrogen and excess of hydrogen; the amount of the latter is estimated by exploding with excess of oxygen when two-thirds of the diminution in volume represents the hydrogen present.

## QUESTIONS.—CHAPTER XVII.

- 1 How do you account for the occurrence of oxides of nitrogen, and the oxyacids or salts of these, in the air and in the soil?
- 2 What is the effect of distilling (a) very dilute nitric acid, (b) pure nitric acid?
3. Describe an experiment by which oxygen gas can be obtained from nitric acid.
4. Give striking experiments calculated to illustrate in regard to nitric acid, (a) its powerful oxidising action; (b) its powerful solvent action.
- 5 What explanations have been given of the action of dilute nitric acid on copper?
6. Compare the action of nitric acid of different strengths on the metals, zinc, copper and tin. Give equations.
7. Explain what is meant by the *passive state*.
8. What is *aqua regia*, and on what does its special power as a solvent of metals depend?
9. How would you prepare the nitrates of lead and potassium, and obtain them in the form of crystals?
10. Give an account of the action of heat on metallic nitrates.
11. Describe three tests which are characteristic of nitrates.
12. What are the chief uses of nitric acid?
13. What is the action of heat on a solution of nitrous acid?
14. Give examples (with equations) of (a) the oxidising action, (b) the reducing action of nitrous acid.
15. By what chemical reactions may nitrites be distinguished from nitrates?
16. What is the action of chlorine on dry silver nitrate?
17. How is nitric anhydride usually prepared, and what are its chief properties?
18. How is the tetroxide of nitrogen obtained? Discuss the action of heat on this substance
19. Under what conditions does nitrogen peroxide become a supporter of combustion?

20. What is the action of water on nitrogen peroxide?
21. Under what conditions does nitrogen trioxide exist, and how is it prepared?
22. How may *pure* nitric oxide be obtained?
23. What are the properties of nitric oxide, and how may it be distinguished from nitrous oxide?
24. Demonstrate that the chemical formula of nitric oxide is NO.
25. Give two methods for the preparation of nitrous oxide.
26. State the *physical* properties of nitrous oxide, and say how you would distinguish by chemical tests nitrous oxide from oxygen. In what respects does it resemble oxygen?



## CHAPTER XVIII.

### SULPHUR. SULPHURETTED HYDROGEN.

#### SULPHUR.

209. **Occurrence**—Sulphur is one of the comparatively few elements which occur in quantity in the uncombined condition. In Europe it is found in the neighbourhood of active or extinct volcanoes in Italy, Sicily, Iceland, etc., being usually associated with mineral matter. In combination with hydrogen it is found as sulphuretted hydrogen in certain mineral springs, and with metals as mineral sulphides, such as iron pyrites,  $\text{FeS}_2$ ; galena,  $\text{PbS}$ ; zinc blende,  $\text{ZnS}$ ; and cinnabar,  $\text{HgS}$ . Sulphates of lime (gypsum) and barium (heavy spar) also occur in some localities in considerable quantity. We see then that sulphur either free or in combination is widely distributed.

210. **Extraction**.—Sulphur melts at  $115^\circ \text{C}$ ., and in the molten condition can be run off from the earthy impurities and obtained in a state of moderate purity. The process is carried out as follows.—Impure native sulphur is stacked in a brick kiln on a sloping floor, vertical air spaces being left at intervals. The sulphur is lighted at the bottom, a small quantity burns and the heat produced melts out the rest. The melted sulphur runs down the sloping floor and collects in a trough placed to receive it.

Sulphur boils at  $440^{\circ}\text{C}$ , giving off brownish-red vapours which readily condense again on cooling, and the further purification of the sulphur may be effected by distillation in an iron retort, the vapours being passed into a brick chamber where they condense. (Fig. 54) At the outset when the chamber is cool the product obtained is a fine powder, called "flowers of sulphur," for just as water

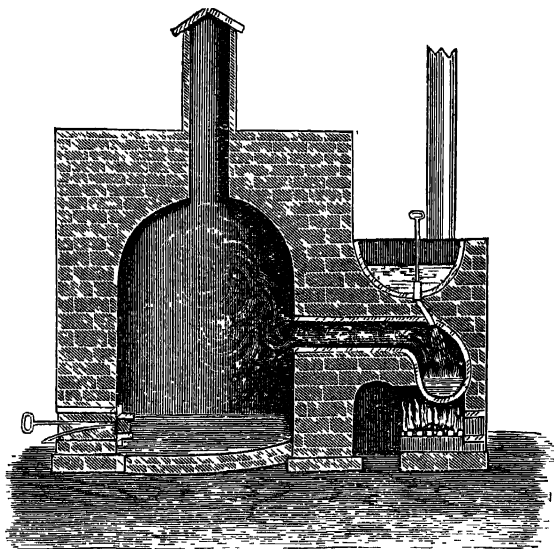


FIG 54.

vapour at temperatures below zero (the melting-point of ice) condenses in the form of snow, so in the case of sulphur there is formed by rapid cooling finely-divided sulphur.

When the temperature of the chamber rises above the melting-point of sulphur ( $115^{\circ}\text{C}$ .), the product of the condensation is *liquid* sulphur, and this is run off into moulds where it is cast into sticks known familiarly as "brimstone."

## 211. Physical changes of Sulphur under the action of Heat.

**Exp 144**—Put about 30 grammes of sulphur in a wide test-tube, and heat it as evenly as possible in the flame of a Bunsen burner. At  $115^{\circ}\text{C}$  it will be seen to melt, and at a slightly higher temperature it forms a limpid liquid of a pale yellow colour. As it gets hotter the liquid grows more viscid and darker in colour, till at  $250^{\circ}\text{C}$ . it becomes almost solid and nearly black. Above  $250^{\circ}\text{C}$  it again becomes more mobile, and at  $440^{\circ}\text{C}$ . it boils and gives off a brownish-red vapour. Pour some of the sulphur at about  $350^{\circ}\text{C}$ . in a thin stream into a beaker of water, and note the production of plastic sulphur.

**212. Allotropic modifications of Sulphur.**—Sulphur exists in several forms which show marked differences in their physical properties. These may be classified as follows:—

(a) Crystalline forms:

- (1) Octahedral sulphur.
- (2) Prismatic sulphur.

(b) Amorphous forms:

- (1) Plastic sulphur.
- (2) White amorphous sulphur.
- (3) Yellow amorphous sulphur.

(c) Colloidal sulphur.

**Octahedral Sulphur.**—Sulphur is found naturally in rhombic octahedra (see Fig. 55), and it is in this form that it separates out from solvents, such as bisulphide of carbon, on slow evaporation. The specific gravity of rhombic sulphur is 2.045.

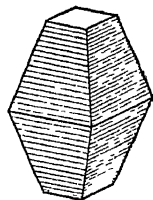


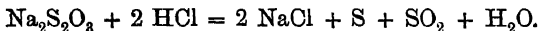
FIG 55.

**Prismatic Sulphur.**—Sulphur in this form is no longer rhombic, but monoclinic; it is also of lower specific gravity, 1.93, and melts at  $120^{\circ}$  instead of  $115^{\circ}$ , and when left at the ordinary temperature for some time, breaks up and passes into the more stable rhombic form, as, indeed, all the modifications tend to do. It is soluble in carbon bisulphide.

**Exp 145.**—Melt about 500 grammes of sulphur in a clay crucible, and allow it to cool until a crust forms at the surface; the crust is then pierced and the still liquid portion poured out. Beneath the crust and on the sides of the crucible will be found long prismatic needles of sulphur.

**Plastic Sulphur.**—As already stated, this form of sulphur is obtained by pouring sulphur at a temperature of  $350^{\circ}\text{C}$ . into cold water. Whilst in the crystalline form sulphur is brittle, in this condition, as the name implies, it can be moulded with the fingers, or drawn out into long flexible threads. Unlike the modifications previously described, it is insoluble in carbon disulphide: its specific gravity is 1.95. On standing, it slowly hardens and passes into the ordinary form of sulphur.

**White Amorphous Sulphur.**—When hydrochloric acid is added to a solution of a polysulphide, *e.g.* calcium polysulphide or yellow ammonium sulphide, a white very finely-divided precipitate of amorphous sulphur is produced, called “milk of sulphur.” This precipitate is insoluble in carbon bisulphide. If sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) is used instead of a polysulphide, a similar white precipitate of sulphur is at first produced, but this gradually turns yellow, when it becomes soluble in carbon bisulphide (being converted into the crystalline rhombic variety)—



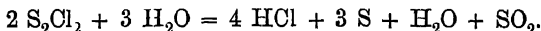
**Exp 146.**—Make a moderately concentrated solution of sodium thiosulphate, or of an alkaline polysulphide (*e.g.* solution of yellow ammonium sulphide), and add a few drops of hydrochloric acid. The solution becomes turbid, and a white precipitate of “milk of sulphur” is produced.

Note that in the case of the thiosulphate the precipitate gradually turns yellow. Now add some carbon bisulphide and shake up; the yellow crystalline precipitate dissolves, leaving a white precipitate of unchanged amorphous sulphur.

This variety of sulphur has a specific gravity 1.82.

**Yellow Amorphous Sulphur.**—“Flowers of sulphur” obtained as already described consists chiefly of small crystals of octahedral sulphur, but also contains a small

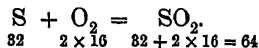
percentage of an amorphous modification. The latter is insoluble in carbon bisulphide, and can therefore be obtained by treating flowers of sulphur with this liquid, when the octahedral sulphur dissolves, and the amorphous portion remains behind as a light yellow powder of specific gravity 1.96. This form is also produced when sulphur dichloride ( $S_2Cl_2$ ) is decomposed by water—



**Colloidal Sulphur** is soluble in water and is obtained when solutions of sulphuretted hydrogen and sulphur dioxide are mixed—



**213. Proof that the Allotropic Modifications of Sulphur consist of the same Element.**—On burning a known weight of any form of sulphur in oxygen and weighing the sulphur dioxide produced, it is found that in all cases the ratio of the weight of sulphur dioxide formed to that of sulphur burnt is 64 : 32, which agrees with the equation—



This proves that each of the different forms consists wholly of the same element. The experiment may be carried out as follows:—A small fragment of sulphur (about 0.2 gramme) is weighed out accurately in a porcelain "boat" (A, Fig 56). This is introduced into a piece of hard glass tubing in the position shown in the diagram. A series of bulbs, B, containing strong caustic potash solution, are weighed together with a small calcium chloride tube C, and then attached to the end of the tube remote from the porcelain boat. The other end of the tube is connected with a supply of dry oxygen. The boat is now gently heated by means of a Bunsen burner, and a slow current of oxygen is passed through the tube. The sulphur burns forming sulphur dioxide, which is absorbed in the potash bulbs. Any moisture driven out of the bulbs by the current of gas is

absorbed by the calcium chloride in C, which, it will be remembered, was weighed along with the bulbs, thus an error in the final weight of the bulbs due to loss of water vapour is avoided. When all the sulphur has disappeared, and no more absorption is observed to be taking place in the bulbs, they are disconnected and re-weighed (along with the calcium chloride tube), after allowing them to cool. The increase in weight gives the weight of sulphur dioxide. If any sulphur vaporises and condenses in the cooler part of the tube this must be gently heated by a Bunsen burner till it becomes oxidised.

**214. Combination of Sulphur with other elements —** Sulphur combines with many elements when heated with them. Thus it burns in oxygen at about  $400^{\circ}\text{C}$ ., and it

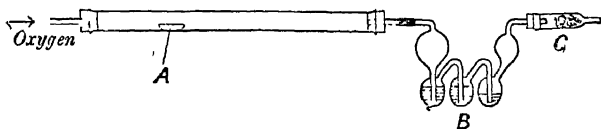


FIG. 56.

combines with carbon at a red heat, forming carbon disulphide,  $\text{CS}_2$ , while chlorine and hydrogen passed into boiling sulphur give sulphur monochloride,  $\text{S}_2\text{Cl}_2$ , and sulphuretted hydrogen respectively.

Many metals combine with sulphur when heated with it; for example, iron (see Exp 64), silver, forming silver sulphide,  $\text{Ag}_2\text{S}$ , and copper, forming cuprous sulphide,  $\text{Cu}_2\text{S}$ .

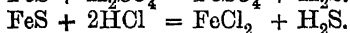
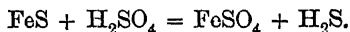
**Exp. 147.**—Heat sulphur to the boiling-point and until the upper part of the tube is filled with its vapour, and then plunge into it thin sheet copper, or Dutch metal, the metal glows, and enters into combination with the sulphur to form sulphide of copper.

**215 Uses of Sulphur.**—Sulphur is largely used in the arts for the production of matches, gunpowder, sulphuric acid, and as a source of sulphurous acid for bleaching wool, straw and silk.

SULPHURETTED HYDROGEN,  $\text{H}_2\text{S}$ 

216. **Occurrence.**—Sulphuretted hydrogen occurs in solution in certain mineral waters (*e g* those at Harrogate), and is formed during the putrefaction of animal and vegetable matters which contain sulphur.

217. **Preparation.**—The gas is most conveniently prepared by the action of dilute sulphuric acid, or dilute hydrochloric acid on ferrous sulphide—



The best form of apparatus to use when a continuous supply of the gas is required is that shown in Fig 57. The

upper bottle contains the dilute acid, and the lower one the ferrous sulphide in lumps about the size of a walnut. The two bottles are connected by rubber tubing, on which is placed a clip, A. The mouth of the lower bottle is fitted with a cork, through which passes a delivery tube provided

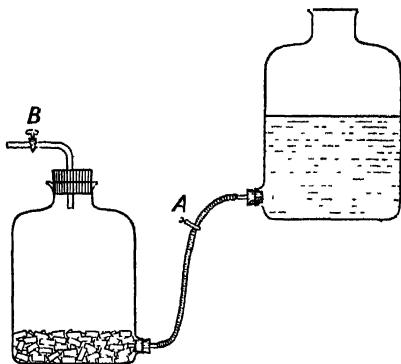


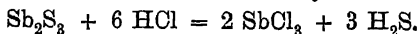
FIG. 57.

with a stopcock, B, which is kept closed except when a supply of the gas is required. When this is the case the clip is loosened and a little acid allowed to run down on to the ferrous sulphide; the gas is led away by the delivery tube and passed through a wash-bottle containing a little water to remove impurities. To stop the supply of gas B is closed, and the ferrous sulphide bottle is raised so that

the acid in it flows back into the acid bottle  $\text{H}_2\text{S}$  cannot be collected over cold water as it is too soluble; and owing to its offensive nature, and to the fact that it is only slightly heavier than air, it should not be collected by displacement of air, also mercury is inadmissible because it attacks the gas. Since, however, the solubility in water rapidly decreases with rise in temperature, *hot* water may be used.

If only a small quantity of sulphuretted hydrogen is required, a Wolff's bottle provided with a thistle funnel and delivery tube may replace the apparatus above described.

The gas obtained in this way always contains free hydrogen on account of the iron present in the ferrous sulphide (which is prepared by heating iron and sulphur together). To obtain *pure* sulphuretted hydrogen, sulphide of antimony is heated in a flask with *concentrated* hydrochloric acid—

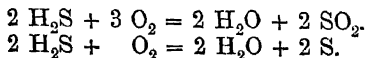


Antimony chloride.

The gas is passed through a wash-bottle containing water to remove hydrochloric acid, and may then be collected as before. If *dry* sulphuretted hydrogen is required, the gas, after washing, should be passed through a U-tube containing calcium chloride to absorb the water vapour (sulphuric acid cannot be used because it reacts with the gas).

Sulphuretted hydrogen is also produced when hydrogen and sulphur vapour are passed together through a red-hot tube.

**218. Properties.**—Sulphuretted hydrogen is a colourless gas with a disagreeable odour, and is poisonous if inhaled in quantity. It is moderately soluble in water, which at  $0^\circ \text{C}$ . and 760 mm pressure dissolves 4.37 times its volume of the gas, and at  $20^\circ$ , 2.9 times its volume. The aqueous solution possesses the characteristic smell of the gas, and has a faintly acid reaction. Sulphuretted hydrogen burns with a blue flame, forming water vapour and sulphur dioxide in a free supply of oxygen or air, whilst in a limited supply of air free sulphur is formed—





**Exp. 148.**—Prepare sulphuretted hydrogen by the action of dilute sulphuric acid on ferrous sulphide, wash the gas by passing through a little water contained in a flask, and collect a cylinder over hot water. Apply a lighted taper to the mouth, and note that the gas burns with a pale blue flame, and that a gas ( $\text{SO}_2$ ) is formed which has the suffocating odour of burning sulphur. There is usually a slight deposit of sulphur on the sides of the vessel due to the cooling of the gas, and the difficulty of access of air in sufficient quantity to ensure complete combustion.

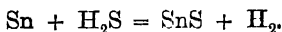
If the taper be passed within the cylinder in which the gas is burning, it will be extinguished, showing that sulphuretted hydrogen, like hydrogen, burns in air (or oxygen), but does not support the combustion of a taper.

Whilst performing this experiment you will have noticed the obnoxious odour of the gas

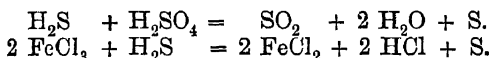
**Exp 149.**—Fit the generating apparatus with a tube about 20 centimetres long, drawn out to a fine jet. The gas may be lighted at the jet when all the air is expelled, and the presence of water in the products of combustion may be shown by holding a cool glass vessel over the flame. Also, by depressing the lid of a porcelain crucible into the flame, a deposit of sulphur may be obtained. Now heat the tube some distance away from the orifice with a Bunsen burner or spirit-lamp, and the gas will be decomposed by the heat, and a deposit of sulphur will form a little beyond the point where the heat is applied. Finally, extinguish the flame, and allow the gas to impinge on a piece of filter-paper moistened with nitrate (or acetate) of lead, a dark stain will be produced owing to the formation of sulphide of lead. By this test the presence of sulphuretted hydrogen may be detected even when present in very small quantities.

We have seen in the experiment just performed that sulphuretted hydrogen is easily decomposed by heat. It is also very readily broken up by the action of metals, many of which act upon it even at ordinary temperature; the metal combines with the sulphur, and free hydrogen is liberated. The tarnishing of silver when exposed to the air of towns is an example of this; the air contains a small percentage of sulphuretted hydrogen produced during the combustion of coal, which usually contains a small quantity of iron pyrites ( $\text{FeS}_2$ ); this  $\text{H}_2\text{S}$  in the air attacks the silver, producing a layer of silver sulphide, which is black. On heating many metals in the gas the same change is brought about much more rapidly; tin and cadmium, for instance, very readily bring about the complete decom-

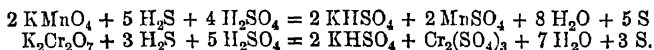
position of a confined volume of the gas on the application of gentle heat—



As might be expected from the ease with which the gas is decomposed with liberation of hydrogen, sulphuretted hydrogen belongs to the class of reducing agents. For example, it reduces sulphuric acid to sulphur dioxide, and ferric chloride to ferrous chloride, according to the equations—



Again, potassium permanganate and potassium bichromate in the presence of dilute sulphuric acid are reduced to manganous sulphate and chromic sulphate respectively—



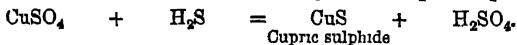
In all these cases free sulphur is liberated. The action of the halogens on the gas has already been referred to in Chap. XIV.

**219. Sulphides.**—The formation of the sulphides of the metals can conveniently be studied by experiment.

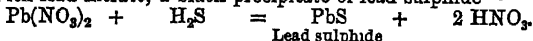
**Exp. 150.**—Make a solution of sulphuretted hydrogen in water, and dip in it a blue litmus paper, it will be slightly reddened, showing that sulphuretted hydrogen is a weak acid. By replacing the hydrogen of the acid by metals sulphides are produced.

Pour a few c.c. of it into neutral solutions of copper sulphate, lead nitrate, nickel sulphate, zinc sulphate, calcium chloride, sodium chloride. The following results will be noticed :—

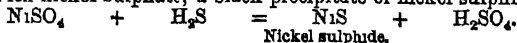
With copper sulphate, a black precipitate of cupric sulphide—



With lead nitrate, a black precipitate of lead sulphide—



With nickel sulphate, a black precipitate of nickel sulphide—



With zinc sulphate, a white precipitate of zinc sulphide—  

$$\text{ZnSO}_4 + \text{H}_2\text{S} = \underset{\text{Zinc sulphide}}{\text{ZnS}} + \text{H}_2\text{SO}_4.$$

The same effects are produced by passing  $\text{H}_2\text{S}$  gas into solutions of the above salts

In the case of calcium chloride and sodium chloride there will be no precipitate, owing to the fact that the sulphides of calcium and sodium are readily soluble in water.

Now add some hydrochloric acid to the tubes containing the precipitates, and the sulphides of nickel and zinc will be found to dissolve, whilst those of copper and lead will remain

By such a method we may prepare many of the sulphides of the metals, and we shall find them divisible into the following classes—

- (1) Sulphides insoluble in water and dilute mineral acids.
- (2) Sulphides which are insoluble in water, but soluble in dilute mineral acids
- (3) Sulphides which are soluble even in water.

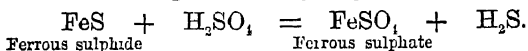
The precipitate may be separated by filtration from the solution which remains, and it is possible in this way to separate any member or members of one of these classes from those of another class.

Many of the sulphides may also be prepared by mixing the metal (preferably in a finely-divided condition or in filings) intimately with excess of powdered sulphur and heating in a porcelain crucible until the portion of sulphur over and above that which will enter into combination with the metal is volatilised. Access of air or of gases which may act upon the sulphide is to be avoided.

When strong aqueous ammonia is saturated with sulphuretted hydrogen the product consists of a solution of ammonium sulphide  $(\text{NH}_4)_2\text{S}$ , ammonium hydrogen sulphide,  $\text{NH}_4\cdot\text{HS}$ , and ammonium hydroxide; this solution is known as "ammonium sulphide." On allowing it to stand in contact with the air it undergoes partial oxidation with formation of free sulphur, which then combines with more ammonium sulphide to form polysulphides of the general formula  $(\text{NH}_4)_2\text{S}_x$ , where  $x$  may be as high as 9. These polysulphides are yellow, and so the solution of ammonium sulphide which is colourless at first gradually turns yellow and is then known as "yellow ammonium

sulphide." Yellow ammonium sulphide is largely employed as a reagent in qualitative analysis.

**220 Tests for Sulphides**—(1) Warm the substance with dilute sulphuric acid, *most* sulphides are decomposed with the evolution of sulphuretted hydrogen, *e. g.*—



The sulphuretted hydrogen may be detected by its odour or by its action on paper moistened with a solution of acetate of lead,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ .

(2) Mix a little of a dry sulphide with sodium carbonate and heat strongly on charcoal with the blowpipe flame. Sulphide of sodium is formed, and may be recognised by the fact that when a little of the product is placed on a silver coin and moistened, a brown stain is produced. All sulphides react in this way.

**221. Composition of Sulphuretted Hydrogen**—When sulphuretted hydrogen is heated alone or with metallic tin it yields its own volume of hydrogen. (If tin is used the experiment may conveniently be carried out in the apparatus shown in Fig 53, § 208.) Applying Avogadro's hypothesis it follows that one molecule of sulphuretted hydrogen yields and contains one molecule, *i. e.* two atoms, of hydrogen. As yet we have not determined the number of atoms of sulphur in the gas. Call this number  $x$ ; then the formula for sulphuretted hydrogen may be written  $\text{H}_2\text{S}_x$ . The simplest way to find  $x$  is to determine the molecular weight of sulphuretted hydrogen from its density. It is found that the relative density of the gas is 17 ( $\text{H}=1$ ); the molecular weight is, therefore,  $2 \times 17 = 34$ , and so

Molecular weight of sulphuretted hydrogen	=	34
Weight of hydrogen in a molecule of sulphuretted hydrogen	=	2
“ “ sulphur “ “ “	=	<u>32</u>

But 32 is the atomic weight of sulphur; hence the molecule of sulphuretted hydrogen contains one atom of sulphur, *i. e.*  $x=1$ , and the formula becomes  $\text{H}_2\text{S}$ .

## QUESTIONS — CHAPTER XVIII.

- 1 How is sulphur separated from the mineral matter with which it is associated in the native condition?
2. Under what conditions are "flowers" of sulphur and "milk" of sulphur formed?
3. Describe the physical changes through which sulphur passes when it is heated in the absence of air.
4. Tabulate the properties of the different allotropic modifications of sulphur so as to bring out the differences between them.
- 5 Describe the preparation of (a) prismatic sulphur, (b) plastic sulphur.
6. What is the action of sulphur vapour on heated copper, iron, oxygen, hydrogen and chlorine respectively? Give equations representing the changes which occur.
- 7 How would you prove that octahedral and prismatic sulphur consist of the same element?
- 8 How would you prepare and collect a specimen of *pure dry* sulphuretted hydrogen?
9. What products are obtained by burning sulphuretted hydrogen (a) in a limited supply of air, (b) in excess of air?
10. Give examples with equations of the reducing action of sulphuretted hydrogen.
- 11 What is the action of sulphuretted hydrogen on acid solutions of (a) silver nitrate, (b) copper sulphate, (c) lead nitrate? Give equations showing the changes which take place.
12. How would you show (a) that sulphuretted hydrogen contains hydrogen and sulphur, (b) that it contains these elements in the proportions represented by the formula  $H_2S$ ?
13. What is the composition of "yellow ammonium sulphide"?

## CHAPTER XIX.

### OXIDES AND OXYACIDS OF SULPHUR.

222 SULPHUR forms four compounds with oxygen, namely, sulphur dioxide,  $\text{SO}_2$ , sulphur trioxide,  $\text{SO}_3$ , sulphur sesquioxide,  $\text{S}_2\text{O}_3$ , and sulphur heptoxide,  $\text{S}_2\text{O}_7$ . Two of these oxides,  $\text{SO}_2$  and  $\text{SO}_3$ , combine with water to produce corresponding acids, sulphurous acid,  $\text{H}_2\text{SO}_3$ , and sulphuric acid,  $\text{H}_2\text{SO}_4$ , and they are therefore the anhydrides of these acids. The other two oxides do not produce the corresponding acids on treatment with water, though these acids can be obtained by other methods. The full list of the oxyacids of sulphur is—

Sulphurous acid	$\text{H}_2\text{SO}_3$
Sulphuric acid	$\text{H}_2\text{SO}_4$
Nordhausen sulphuric acid	$\text{H}_2\text{S}_2\text{O}_7$
Thiosulphuric acid	$\text{H}_2\text{S}_2\text{O}_3$
Hyposulphurous acid	$\text{H}_2\text{S}_2\text{O}_4$
Persulphuric acid	$\text{H}_2\text{S}_2\text{O}_8$
Dithionic acid	$\text{H}_2\text{S}_2\text{O}_6$
Trithionic acid	$\text{H}_2\text{S}_3\text{O}_6$
Tetrathionic acid	$\text{H}_2\text{S}_4\text{O}_6$
Pentathionic acid	$\text{H}_2\text{S}_5\text{O}_6$
Hexathionic acid	$\text{H}_2\text{S}_6\text{O}_6$

We shall only study the more important of these compounds, viz. sulphur dioxide, sulphur trioxide, sulphurous acid, sulphuric acid and thiosulphuric acid.

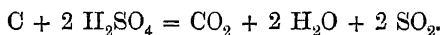
SULPHUR DIOXIDE,  $\text{SO}_2$ .

**223. Preparation**—When sulphur burns in air or oxygen, sulphur dioxide is formed, and for purposes in which admixture with nitrogen or the excess of oxygen is of no moment, the gas may be prepared by this method. On the manufacturing scale indeed sulphur dioxide is sometimes so obtained, though more usually a sulphide containing a large proportion of sulphur, such as iron pyrites,  $\text{FeS}_2$ , is employed (see § 232).

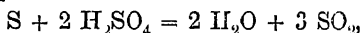
When the gas is required in a tolerably pure condition the following method is applicable.—

**Exp 151**—About 20 grammes of metallic copper are placed in an eight-ounce flask provided with a thistle funnel and delivery tube, and 50 c.c. of concentrated sulphuric acid are poured down the funnel. The flask is then heated on a sand bath, moderating the heat so soon as the action commences. The reaction which takes place is a complex one, but consists essentially in the reduction of the sulphuric acid by copper. The latter is converted chiefly into  $\text{CuSO}_4$  and  $\text{Cu}_2\text{S}$ .

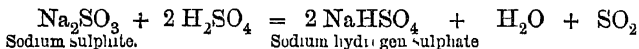
Mercury, charcoal, or sulphur may be substituted for copper, but in the case of charcoal the gas which passes off is mixed with carbon dioxide:—



With sulphur the reaction is—



sulphur dioxide being formed both from the sulphur itself and from the sulphuric acid used. It remains to be added that all sulphites when treated with a mineral acid yield sulphur dioxide—



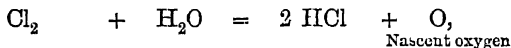
Sulphur dioxide being very soluble in water cannot be collected over this liquid, mercury may however be used, but as the gas is more than twice as heavy as air it may be conveniently collected by displacement of air. Several jars may be filled with it, and its properties demonstrated by the experiments given below.

**224. Properties.**—Sulphur dioxide is a heavy colourless gas having a suffocating odour. At 760 mm. pressure water at zero dissolves 80 times its volume of the gas, and at 10° C. 56 times its volume, the solution having an acid reaction. Sulphur dioxide condenses to a liquid under ordinary atmospheric pressure at -8° C, and under 2 atmospheres pressure at 0° C. It can therefore be obtained in the liquid form by passing the gas into a vessel surrounded by a freezing mixture of ice and salt.

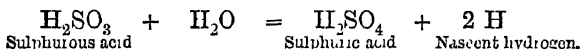
**Exp 152** —Put a lighted taper into a jar of the gas, it will be extinguished, nor will the gas itself burn. Metallic potassium when previously ignited will however burn at the expense of the oxygen in this gas.

**Exp 153.**—Show the great solubility of the gas by the method used in Experiment 118 (§ 149), or by passing the gas through 10 c.c. of water until a saturated solution is obtained. Note the acid properties of the solution, and that it possesses the odour of the gas.

**225 Reducing action of Sulphur Dioxide**—Sulphur dioxide is a strong reducing agent, its powers as an antiseptic and as a medium for bleaching silk, straw and wool are due to its affinity for oxygen. Chlorine bleaches in consequence of its bringing about the oxidation of the colouring matter, sulphur dioxide bleaches, on the contrary, in consequence of its reducing action. The one liberates *oxygen* from water—



the other liberates *hydrogen*—



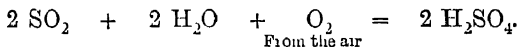
The nascent hydrogen produced then combines with the colouring matter to produce a colourless compound. In many cases the colour is restored by exposure to air, when the oxygen of the air oxidises the colourless compound back to the original coloured substance. In some cases of bleaching by sulphur dioxide the coloured compound *combines directly with SO<sub>2</sub>*, in such cases the colour may be restored by the addition of an acid which decomposes the



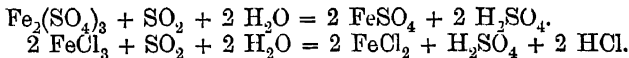
colourless addition product with evolution of sulphur dioxide. The  $\text{SO}_2$  addition product may also be acted upon by the oxygen and moisture of the air, whereby the  $\text{SO}_2$  is converted into sulphuric acid and the coloured compound again set free

**Exp 154**—Throw some rose-leaves into a solution of sulphur dioxide, they are bleached. Now add a few drops of strong sulphuric acid, the colour is restored. Bleach some more of the leaves in the same manner, remove them from the solution, and leave them exposed to the air for some time. The colour will gradually return.

It must be noted that an aqueous solution of sulphur dioxide does not undergo decomposition in the complete absence of air or other oxidising agent, water and sulphur dioxide do not react to give sulphuric acid and hydrogen unless there is some substance present to take up the hydrogen. In the presence of air the solution gradually absorbs oxygen, and the following change takes place—



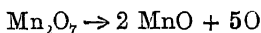
Another good example of the reducing action of sulphur dioxide is its power of converting ferric salts into ferrous salts. Thus ferric sulphate is reduced to ferrous sulphate, and ferric chloride to ferrous chloride—



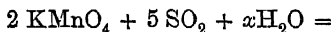
Potassium permanganate and potassium chromate are also readily reduced, the change being rendered conspicuous by the alterations in colour which result, the purple permanganate being decolorised, and the yellow chromate turned green.

**Exp 155**—Add a solution of sulphur dioxide in water to solutions of potassium permanganate and potassium chromate respectively. Note the colour changes; they may be used as tests for sulphur dioxide, both in the gaseous state and in solution. Potassium chromate is more usually employed for this purpose than potassium permanganate.

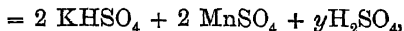
**226 How to work out an Equation**—It will be useful to discuss the mode of arriving at the equations which express the reactions taking place. Taking the case of potassium permanganate we know that the substances we start with are  $\text{KMnO}_4$ ,  $\text{SO}_2$ , and water, and the products are acid potassium sulphate,  $\text{KHSO}_4$  (not the normal sulphate, because free sulphuric acid is produced), manganese sulphate,  $\text{MnSO}_4$ , and free sulphuric acid. Now potassium permanganate may be considered as made up of the two oxides,  $\text{K}_2\text{O}$  and  $\text{Mn}_2\text{O}_7$  ( $\text{K}_2\text{O} + \text{Mn}_2\text{O}_7 = \text{K}_2\text{Mn}_2\text{O}_8 = 2 \text{KMnO}_4$ ), and manganese sulphate of  $\text{MnO}$  and  $\text{SO}_3$ . We may therefore represent the reduction of potassium permanganate to manganese sulphate by reference to the corresponding oxides of manganese, thus—



But  $\text{Mn}_2\text{O}_7$  corresponds to two molecules of potassium permanganate, and therefore *two molecules of*  $\text{KMnO}_4$  *yield five atoms of oxygen available for oxidising purposes*, i.e. of so-called “available oxygen.” Now, one molecule of sulphur dioxide requires one atom of oxygen to convert it into sulphur trioxide, the oxide corresponding to sulphuric acid, consequently 5 atoms of oxygen will oxidise 5 molecules of sulphur dioxide. We can now write down the left-hand side of the equation with the exception of an unknown quantity of water, say  $x$  molecules—

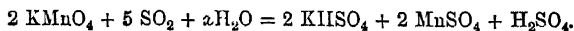


Now since the potassium goes to  $\text{KHSO}_4$  and the manganese to manganese sulphate, the right-hand side of the equation may be written—

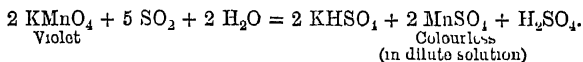


where  $y$  has to be determined.

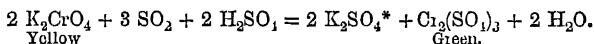
It is easy to see that  $y = 1$ , for only one atom of sulphur of the 5  $\text{SO}_2$  remains to be accounted for. So far then we may write the equation—



But on the right side of the equation we have four atoms of hydrogen, and in order that the left-hand side may have the same number we must make  $x = 2$ . The correct equation is, therefore—

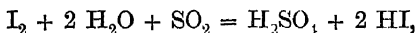


In the case of potassium chromate there is not enough sulphuric acid produced to convert all the potassium and chromium into sulphates, so that some free sulphuric acid must be added. Reasoning in a similar manner to that adopted above the equation representing the reaction is found to be—

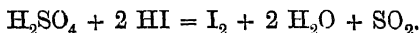


**227. Action of Sulphur Dioxide on Iodine—Reversible actions**—Iodine is reduced to hydriodic acid by sulphur dioxide in the presence of water, but the reaction ceases when a small quantity of hydriodic acid has been produced, owing to the tendency of the latter to reduce sulphuric acid, *i.e.* for the reaction to proceed in the reverse direction. This is an example of a *reversible action*, the exact course of the reaction depending on the *relative masses* of the reacting substances (other conditions remaining the same).

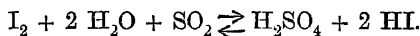
The direct reaction is thus represented—



and the reverse reaction is, of course—



To indicate that the change is reversible it is often expressed thus—



$\text{KHSO}_4$  will be produced if *excess* of sulphuric acid is added.

When the direct and inverse reactions are proceeding at the same rate no further change will apparently take place, though there is no reason for supposing that the reactions cease altogether, they merely continue at equal rates, some molecules of iodine being reduced, whilst some molecules of hydriodic acid are oxidised

**Exp 156** —Liberate iodine from potassium iodide by adding a *few drops* of chlorine water, now add an aqueous solution of sulphur dioxide, and the brown colour of the iodine will disappear.

### 228 Composition of Sulphur Dioxide—This may be

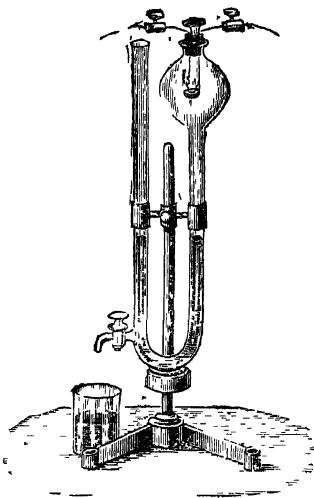


Fig 58.

determined by synthesis By means of the arrangement shown (Fig 58), a fragment of sulphur may be burnt in oxygen The sulphur is fused on to thin platinum wire, and ignited by passing an electric current along the wire, by which the wire is heated. The apparatus and the oxygen used in the experiment must be free from moisture. The gas in the globe at first expands owing to the heat of combustion, and

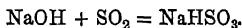
forces the mercury up the further limb, but on cooling it returns to its original volume It is seen therefore, that during the combination of sulphur and oxygen to form sulphur dioxide no alteration in volume occurs, that is to say, *sulphur dioxide contains its own volume of oxygen* It follows then from Avogadro's hypothesis

that one molecule of sulphur dioxide must contain one molecule of oxygen. Further, since the molecular weight of the gas as found from its density is 64, the composition, deduced by a method similar to that used for sulphuretted hydrogen (see § 221), must be represented by the formula  $\text{SO}_2$ .

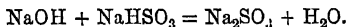
**229. Sulphurous Acid and Sulphites**—We have seen that sulphur dioxide dissolves readily in water, forming an acid,  $\text{H}_2\text{SO}_3$ . This acid has never been isolated from its dilute aqueous solution, any attempt to concentrate the solution resulting in decomposition with loss of sulphur dioxide. Sulphurous acid contains two atoms of hydrogen in its molecule, both of which are replaceable by metals; it is, therefore, a *divalent* acid (see § 87), and gives rise to two series of salts called *sulphites*. The first series in which both atoms of hydrogen are replaced are the *normal* sulphites, e. g.  $\text{Na}_2\text{SO}_3$ ,  $\text{K}_2\text{SO}_3$ ,  $\text{CaSO}_3$ , the second series in which only one hydrogen atom is replaced are the *acid* sulphites, e. g.  $\text{NaHSO}_3$ ,  $\text{KHSO}_3$ ,  $\text{CaH}_2(\text{SO}_3)_2$ .  $\text{NaHSO}_3$  is called by three different names, viz acid sodium sulphite, sodium hydrogen sulphite, and bisulphite of soda, the second regards sulphurous acid as a hydrogen salt, the third is a popular name which has no scientific basis.

The sulphites of the alkali metals may be prepared by passing sulphur dioxide into solutions of the corresponding hydroxides or carbonates.

**Exp 157**—Take 50 c.c. of a solution of caustic soda, and pass sulphur dioxide into it till it is saturated with the gas. On allowing the solution to evaporate at ordinary temperatures (it decomposes when heated), or on adding alcohol to it, the *acid salt*, sodium hydrogen sulphite, separates out—

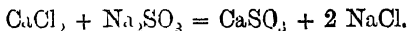


If we add a second 50 c.c. of the same solution of caustic soda we shall then obtain on evaporation or treatment with alcohol the *normal salt*—



In a similar way, substituting caustic potash for caustic

soda, the sulphites of potash may be prepared. The normal sulphites of all metals excepting the alkali metals are insoluble in water, and may be obtained as precipitates by the addition of a soluble salt of the metal to a solution of an alkaline sulphite—



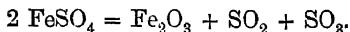
Sulphites slowly take up oxygen from the air, passing into sulphates, and all sulphites are decomposed by acids with evolution of  $\text{SO}_2$ .

### SULPHUR TRIOXIDE, $\text{SO}_3$ .

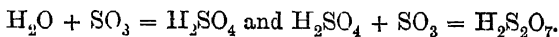
230. This body occurs in small quantity with the sulphur dioxide formed during the combustion of sulphur or iron pyrites.

**Preparation**—Sulphur dioxide and oxygen are passed over platinum sponge, obtained by igniting the double chloride of ammonium and platinum. The gases must be dry, and the platinum sponge gently heated, and there then appear at the exit dense white fumes, which if passed into a cool dry receiver condense to white silky needles of sulphur trioxide.

A second method which is employed in the production of sulphur trioxide in large quantities is based on the decomposition of ferrous sulphate,  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ . This body, when heated, first loses most of its water of crystallisation. The partially dehydrated salt more strongly heated is decomposed thus—

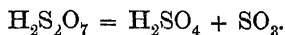


The water which still remains attached to the salt, however, combines with some of the  $\text{SO}_3$  forming  $\text{H}_2\text{SO}_4$ , and this takes up another molecule of  $\text{SO}_3$  forming  $\text{H}_2\text{S}_2\text{O}_7$ —

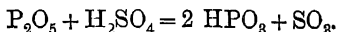


The acid thus produced is known as Nordhausen sulphuric

acid; it differs from ordinary sulphuric acid, in that it fumes when exposed to moist air, and is often termed *fuming sulphuric acid*. This liquid, which condenses from the distillation of partially dehydrated ferrous sulphate, when removed from the receiver and heated, yields the  $\text{SO}_3$  which it has taken up, leaving behind sulphuric acid—



By distilling with a powerful dehydrating agent, such as phosphorus pentoxide, the elements of water may even be removed from sulphuric acid itself, and thus affords a third method whereby  $\text{SO}_3$  may be obtained—



**231. Properties of Sulphur Trioxide.**—At ordinary temperatures sulphur trioxide forms white transparent needles, which melt at  $15^\circ \text{C}$ ., and boil at  $46^\circ \text{C}$ ., at a red heat it breaks up into sulphur dioxide and oxygen. It combines very eagerly with water, evolving much heat, and in contact with water it gives a hissing sound like that of the quenching of hot iron, sulphuric acid is thereby formed. It is of interest to add that sulphur trioxide enters into direct combination with certain metallic oxides, with the production of the corresponding sulphates; for instance, when baryta,  $\text{BaO}$ , and sulphur trioxide are mixed they combine to form barium sulphate,  $\text{BaSO}_4$ , and so much heat is evolved that the mass becomes incandescent.

#### SULPHURIC ACID, $\text{H}_2\text{SO}_4$ .

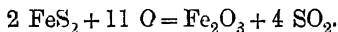
**232. Manufacture.**—We have seen that under certain circumstances sulphur dioxide combines with oxygen to form sulphur trioxide, and that this in presence of water gives sulphuric acid. We have also seen that the oxidation of sulphurous acid to sulphuric acid takes place slowly when its aqueous solution is exposed to air at ordinary temperatures

Such methods are, however, not suitable for the produc-

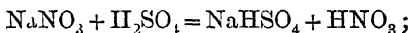
tion of large quantities\* of sulphuric acid as an article of commerce.

The oxidation of sulphurous acid is effectually performed by the intervention of the oxides of nitrogen, and on the large scale sulphur dioxide, oxygen (supplied in the form of air) and steam are brought together, and these in presence of oxides of nitrogen form sulphuric acid

The *sulphur dioxide* in works where a very pure acid is made is obtained by burning brimstone, but in the very large majority of cases iron pyrites is used as the source of the gas. This is burnt in a series of "kilns," and the heat arising from the combustion is sufficient to render the operation continuous, fresh charges being added from time to time—



The *nitric acid* from which the oxides of nitrogen are derived is prepared by the action of concentrated sulphuric acid on Chili saltpetre,  $\text{NaNO}_3$ —



the acid fumes are carried into the flues along which the sulphur dioxide, and air pass, and there intermingle with these gases.

The *air* is drawn in through the pyrites burners or kilns, the draught being maintained by means of a chimney, and by adjustment of the doors of the kilns so as to admit the quantity of air which experience has shown to be necessary.

The *steam* is supplied from low pressure boilers, and introduced into the "chambers" in such a way as to become intimately associated with the other products.

The reaction ending in the production of sulphuric acid does not take place under the circumstances very rapidly, and it is necessary to provide for a lengthened period of

\* Over a million tons of oil of vitriol are produced in Great Britain alone in the course of a year.



contact between the various bodies which take part in it. The gases are led into a series of large chambers where they meet with the steam. These are usually three in number, and have a total capacity of 100,000 to 150,000 cubic feet, the relation of the sulphur burnt to the capacity of the chamber being such that the average time occupied by the gas in traversing the chambers is something like three hours. The walls and floor of the chambers are constructed of sheet-lead supported on a wooden framework, lead being a metal which is scarcely attacked at all

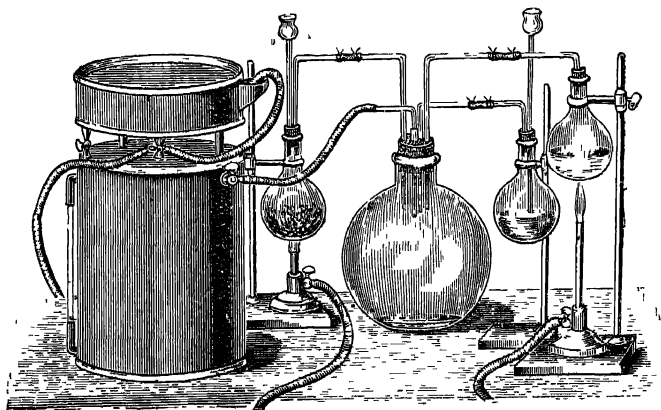


FIG 59.

by sulphuric acid of the strength produced in the chambers. The chambers are kept cool enough to serve as condensers, so that the acid collects on the floor, and is drawn off periodically.

**233. Laboratory representation of the Sulphuric Acid Manufacture**—The formation of sulphuric acid may be represented in the laboratory by taking a large flask (5 litres) and fitting it with a cork provided with five holes through which pass tubes delivering—

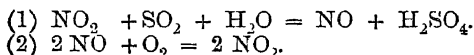
- (1) Sulphur dioxide (for preparation see § 223),
- (2) Nitric oxide ( „ „ „ § 203),
- (3) Steam,
- (4) Oxygen from a gasholder,

while the fifth hole is provided with a tube opening into the air. The arrangement is shown in Fig. 59.

Pass some sulphur dioxide, nitric oxide, steam, and oxygen into the flask, then shut off the steam supply, crystals of nitrosulphonic acid (lead chamber crystals) may be seen to form. On clearing the flask of red fumes by a current of oxygen, and then passing in more steam, these crystals will dissolve with the evolution of red fumes. After allowing the reaction to go on for some minutes, the liquid condensed in the flask may be tested for sulphuric acid (see § 257)

**234. The theory of the Sulphuric Acid Manufacture**—As we have seen (§ 225), sulphur dioxide under the action of air and moisture is transformed into sulphuric acid, but the change takes place very slowly, and the sulphuric acid obtained is extremely dilute. In presence of certain substances, notably the higher oxides of nitrogen as in the sulphuric acid chambers, the conversion is more rapid but much difference of opinion exists as to the actual changes which take place, and even as to the particular oxides of nitrogen which take part in the reaction.

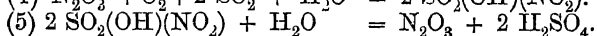
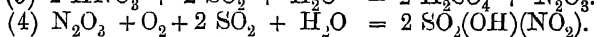
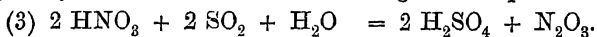
The older theory, originally suggested by Berzelius, regards the nitric oxide (NO) as the body which brings about the formation of the sulphuric acid. This it does by taking up oxygen from the air and forming nitrogen peroxide (NO<sub>2</sub>), which in its turn oxidises the sulphur dioxide, and in presence of steam forms sulphuric acid, being itself reduced again to nitric oxide, the alternate oxidation and reduction going on indefinitely—



It is however observed that if the chambers are insufficiently supplied with steam, white crystals ("lead chamber crystals") are formed, consisting of nitrosulphonic acid,

$\text{SO}_2(\text{OH})(\text{NO}_2)$ . According to the above theory the formation of nitrosulphonic acid is not essential to the process, and does not occur in chambers working normally.

The theory more recently proposed by Lunge, on the other hand, assumes nitrogen trioxide \* to be the true intermediary in the formation of sulphuric acid, and nitrosulphonic acid to be continually formed in the chambers and decomposed again by the excess of steam according to the equations—



Under some conditions, and especially where the gases are just entering the chambers and sulphur dioxide is in large excess, it is, however, admitted that nitric oxide plays a prominent part. With this exception Lunge's theory is not inconsistent with the observations recorded in actual working on the large scale

**235. Properties of Sulphuric Acid.**—The pure concentrated acid is a thick oily liquid (sp. gr 1.84), from whence it derives the name, *oil of vitriol*. It boils at  $338^\circ \text{C}$ , with partial decomposition, so that when the acid containing 100 per cent.  $\text{H}_2\text{SO}_4$  is distilled the residue becomes weaker, until it reaches a strength of about 98.5 per cent.  $\text{H}_2\text{SO}_4$ , at which it remains constant.

It is highly corrosive, charring wood and many organic substances even at the ordinary temperature. This is largely owing to the great avidity with which it takes up water. Wood consists mainly of cellulose, a compound of carbon, hydrogen and oxygen in the proportions in which they are contained in water the acid therefore abstracts water, leaving a mass of carbon.

The methods of preparation of two common gases, ethylene and carbon monoxide, depend upon this same property (see Chaps XXI, XXIII), as does also the employment of concentrated sulphuric acid for drying gases. When sulphuric

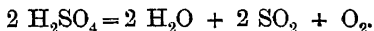
\* The theory holds if  $\text{N}_2\text{O}_3$  be regarded as a mixture of  $\text{NO}_2$  and  $\text{NO}$  (see § 202).

acid and water are mixed a large amount of heat is evolved, again showing the great affinity they possess for one another, and at the same time there is a considerable diminution in volume. The contraction reaches a maximum, viz 8 per cent of the sum of the volumes of acid and water, when the ratio of acid to water corresponds to a hydrate of the formula  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , this probably has a definite existence.

When sulphuric acid vapour is heated to a temperature of about  $450^\circ \text{C}$  it is almost completely dissociated into water and sulphur trioxide; this is shown by the fact that the vapour density is only half what it should be if the molecules consisted of  $\text{H}_2\text{SO}_4$ .

The following considerations will show that the low value of the vapour density proves that dissociation has taken place. Since each molecule of sulphuric acid gives two molecules on dissociation, one of  $\text{H}_2\text{O}$  and one of  $\text{SO}_3$ , it follows from Avogadro's hypothesis that the volume of the dissociation products will be double the volume of the sulphuric acid from which they are derived (on reduction to standard conditions). Consequently the vapour density will be half the theoretical value, which agrees with the experimental result stated above.

When the mixture of water and sulphur trioxide obtained by heating sulphuric acid vapour has its temperature still further raised the sulphur trioxide breaks up into sulphur dioxide and oxygen. Thus, when sulphuric acid is dropped on red-hot bricks it decomposes, as represented in the following equation—



This fact has been utilised as a means of manufacturing oxygen from sulphuric acid on the large scale.

Sulphuric acid is an oxidising agent, though a much weaker one than nitric acid, as we should expect from the smaller percentage of oxygen it contains and the very much higher temperature required to break it up with separation of free oxygen. Thus it is only when *hot and concentrated* that sulphuric acid exhibits oxidising pro-

*vitriol*, because it was obtained by the distillation of green vitriol

The sulphates are remarkable for their tendency to form well-defined crystalline double sulphates, *e.g.* alum,  $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24 \text{H}_2\text{O}$ .

*Insoluble* Sulphates may be obtained by mixing a solution of a soluble salt of the metal whose sulphate is required with a solution of a soluble sulphate, when double decomposition takes place with precipitation of the insoluble salt. The sulphates of lead, calcium, barium and strontium are insoluble or only slightly soluble in water, the rest being readily soluble.

Sulphuric acid, like sulphurous acid, is a dibasic acid and forms two classes of sulphates, the *normal* sulphates such as  $\text{Na}_2\text{SO}_4$ ,  $\text{CaSO}_4$ , and the *acid* sulphates such as  $\text{NaHSO}_4$ , either one or the other being formed according to whether the base or the acid is in excess.

### Test for Sulphates.—

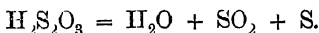
**Exp. 158**—Add barium chloride to a solution which contains either sulphuric acid or a sulphate in presence of hydrochloric acid a white precipitate is formed consisting of sulphate of barium. This is the only common barium salt which is insoluble in water and acids, and the formation of the precipitate is therefore characteristic, and may be taken as a sure indication of the presence of sulphuric acid either in the free state or in combination.

**238. Uses of Sulphuric Acid.**—Sulphuric acid is the most important of all the acids. It is very largely used in the manufacture of other acids, such as nitric and hydrochloric acids, in the manufacture of salt-cake—the first stage in the Leblanc process for the manufacture of washing-soda—and in the conversion of normal calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , into the acid calcium phosphate,  $\text{CaH}_4(\text{PO}_4)_2$ ; the latter is much used for agricultural purposes as a fertiliser, because it is soluble in water, whereas the normal salt is insoluble and so cannot be assimilated by plants. As already mentioned, sulphuric acid is used in the laboratory for drying gases and for the preparation of such gases as

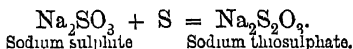
carbon monoxide and ethylene. It is also largely employed in making *storage cells* or *accumulators* for the generation of electric currents.

### THIOSULPHURIC ACID, $\text{H}_2\text{S}_2\text{O}_3$ .

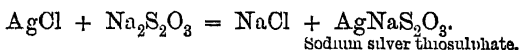
239. Free thiosulphuric acid may be obtained in dilute solution by the action of a mineral acid on a thiosulphate, but it is very unstable, undergoing decomposition according to the equation—



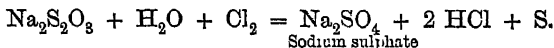
The *thiosulphates* may be obtained by boiling solutions of sulphites with sulphur when direct combination takes place—



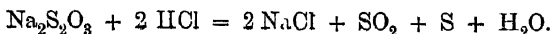
The sodium salt is the most important; it is generally incorrectly called “hyposulphite of soda” or merely “hypo.” It is much used in photography on account of the power it possesses of dissolving the haloid salts of silver, a soluble double thiosulphate of silver and sodium being formed—



Sodium thiosulphate is also used to remove the last traces of chlorine from a fabric which has been bleached, such a substance being termed an *anti-chlor*. This action depends upon the ease with which it is oxidised to sodium sulphate—



**Test for Thiosulphates.**—Thiosulphates in solution are distinguished from sulphites by the fact that with dilute mineral acids they give off sulphur dioxide and also *form a precipitate of finely-divided sulphur*—



## QUESTIONS—CHAPTER XIX.

1. Describe how sulphur dioxide is prepared on the laboratory scale and how it is collected.
2. State the *physical* properties of sulphur dioxide. What volume of the gas will dissolve in 100 c.c. of water at 10° C. under normal pressure?
3. Explain the bleaching action of sulphur dioxide, and show in what respects it differs from that of chlorine.
4. What is the effect of passing chlorine into a solution of sulphur dioxide in water? Give the equation.
5. Express by equations the action of sulphur dioxide on solutions of (1) ferric sulphate, (2) potassium permanganate in the presence of sulphuric acid, (3) potassium chromate in the presence of sulphuric acid.
6. Explain how the equation expressing a complex chemical change (*e.g.* the action of sulphur dioxide on potassium permanganate in the presence of sulphuric acid) may be built up.
7. What is meant by a *reversible action*? Discuss an example.
8. A little chlorine is passed into a solution of potassium iodide, and then afterwards sulphur dioxide is passed in; state the changes which take place and give equations representing them.
9. "Sulphur dioxide contains its own volume of oxygen" Explain the meaning of this statement, and show how you would prove the truth of it by experiment.
10. Describe the preparation of the normal and acid sulphites of soda; what is the action of sulphuric acid on them?
11. Under what circumstances does sulphur dioxide combine directly with oxygen?
12. What is the action of heat on  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ ?
13. How may sulphur trioxide be obtained from (a) Nordhausen sulphuric acid; (b) ordinary sulphuric acid?

14. Describe how sulphur dioxide becomes transformed into sulphuric acid on the large scale; give equations
15. How is sulphur dioxide obtained for the manufacture of sulphuric acid, and what means are employed to ensure its being mixed with the proper quantity of air?
16. Discuss the action of heat on sulphuric acid.
17. Compare the reactions between the metals, zinc, mercury and iron respectively, and (1) dilute sulphuric acid, (2) hot concentrated sulphuric acid
18. What explanations of the action of hot strong sulphuric acid on copper have been suggested?
19. Write down the formulæ of the normal sulphates of copper, potassium, lead, iron and aluminium.
20. Give a method of testing for the presence of a soluble sulphate, and show how you would distinguish whether an aqueous solution contained—
  - (a) free sulphuric acid only,
  - (b) a normal sulphate,
  - (c) a mixture of the two.
21. What are the chief uses of sulphuric acid?
22. What is the correct name for "hyposulphite of soda"? How is this substance prepared, and what are its properties and uses?



## CHAPTER XX.

### PHOSPHORUS.

240. **Occurrence.**—Phosphate of lime,  $\text{Ca}_3(\text{PO}_4)_2$ , the principal source of phosphorus, forms the essential constituent of the mineral apatite, and of bone-ash. The former occurs in the older formations of the earth's crust as—

Chlorapatite,  $3 \text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$ ;  
and Fluorapatite,  $3 \text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ .

Bone-ash is obtained by the dry distillation of bones.

In small quantities phosphates are very widely distributed; all fertile soils contain a small percentage, and they are always found in plants, being, like nitrogen, essential to plant-life.

241. **Manufacture of Phosphorus.**—The first step in the manufacture of phosphorus from bone-ash consists in treating it with sulphuric acid, whereby a double decomposition takes place—



When the decomposition is complete, the product is filtered through cinders, the calcium sulphate remains on the filter, and the phosphoric acid passes through.

The liquid is then concentrated, mixed with charcoal, and further heated almost to dryness, the  $\text{H}_3\text{PO}_4$  losing water and being converted into  $\text{HPO}_3$ —



Finally, the granular product is heated to full redness in clay retorts placed horizontally in series over a fire, when the following reaction takes place—

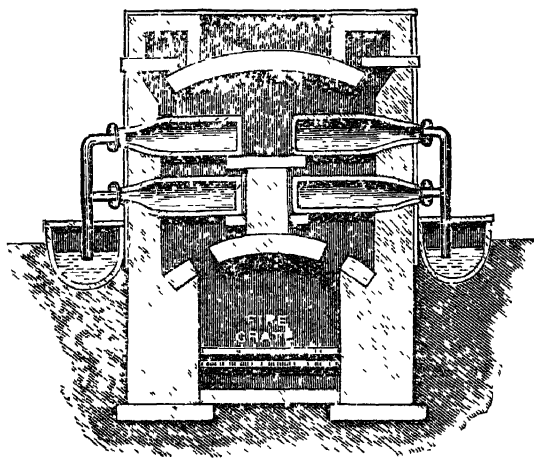
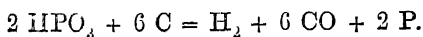


FIG. 60.

Luted into the mouth of each retort is an iron pipe, bent at right angles and dipping into water, the vapour of phosphorus is thus led into the water, and there condensed out of contact with air. The temperature of the water is high enough to keep the phosphorus in the liquid state, and it can be run off or ladled out from time to time. It is further refined by re-melting in water, and filtering through chamois leather or canvas to remove suspended matter, and then finally cast into sticks.

**242. Properties of Phosphorus.**—The phosphorus so obtained is a yellowish, translucent, crystalline solid which can be readily cut with a knife. It has a specific gravity of 1.82, it melts at  $43^{\circ}\text{C}$ , and boils at  $269^{\circ}\text{C}$ . It is insoluble in water, but readily dissolves in bisulphide of carbon.

When phosphorus is exposed to the air it slowly oxidises and emits white fumes (visible in the dark) consisting of a number of oxidation products, namely, phosphorous oxide ( $\text{P}_4\text{O}_6$ ), phosphorous acid ( $\text{H}_3\text{PO}_3$ ), phosphorus pentoxide ( $\text{P}_4\text{O}_{10}$ ), phosphoric acid ( $\text{H}_3\text{PO}_4$ ), and hypophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_6$ ). At the same time the phosphorus becomes faintly luminous. The cause of this luminosity has not been established with certainty, but it is probably connected in some way with the presence of ozone; this substance (along with hydrogen peroxide) is always produced during the slow oxidation of phosphorus, and it has been found that in the presence of bodies such as ether and turpentine, which destroy ozone, the luminosity ceases. At  $34^{\circ}\text{C}$  phosphorus ignites in air and burns with great brilliancy, forming phosphorus pentoxide,  $\text{P}_4\text{O}_{10}$ . On account of the ease with which phosphorus undergoes oxidation it must be kept under water. It should be mentioned that *perfectly dry air* (or oxygen) has no action on phosphorus.

Phosphorus combines also at ordinary temperatures with fluorine, chlorine, bromine, iodine and sulphur, and in the finely-divided condition with oxygen, with the evolution of light and heat.

Phosphorus may be obtained in two other allotropic modifications, red phosphorus, and the recently discovered scarlet phosphorus.

**243 Red Phosphorus** is, according to its method of preparation, a reddish-brown powder or a close-textured mass showing conchoidal fracture. This form is prepared on the large scale by heating ordinary phosphorus at  $250^{\circ}\text{C}$ . in cast-iron pots to which air has only limited access, and removing the unconverted phosphorus which remains by boiling the finely-divided product with caustic

soda solution. On a small scale in the laboratory it may readily be obtained by heating ordinary phosphorus in an atmosphere of nitrogen or carbon dioxide. The amorphous phosphorus differs very considerably in its properties from that already described. It has a higher specific gravity (2.24), and is insoluble in bisulphide of carbon. It undergoes no change in air at ordinary temperatures, and may be freely handled without danger; it combines with oxygen, the halogens, and sulphur at much higher temperatures than ordinary phosphorus. Unlike ordinary phosphorus, it is not poisonous. Red phosphorus was formerly called "amorphous" phosphorus, but it has recently been shown to possess a crystalline structure.

Lucifer matches are tipped with a mixture of phosphorus and certain substances, such as lead dioxide and potassium nitrate, which readily part with oxygen. "Safety" matches contain no phosphorus, being tipped with a mixture of antimony sulphide ( $\text{Sb}_2\text{S}_3$ ), the sulphur being the inflammable body, and potassium chlorate; in this case the match is ignited by rubbing it on a prepared surface of red phosphorus and powdered glass. In either case the heat requisite to promote chemical action and to ignite the phosphorus is generated by friction on a rough surface.

**Scarlet Phosphorus**—This form of phosphorus which has been obtained recently is apparently an amorphous modification of the element.

### HYDRIDES OF PHOSPHORUS.

244. Phosphorus forms three hydrides—

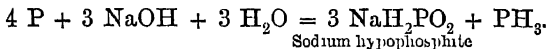
Gaseous phosphoretted hydrogen or phosphine	$\text{PH}_3$ .
Liquid phosphoretted hydrogen	... .. $\text{P}_2\text{H}_4$ .
Solid phosphoretted hydrogen	... .. $\text{P}_4\text{H}_2$ .

The only one of these compounds which we shall consider is the gaseous hydride  $\text{PH}_3$ , the others being unimportant.

PHOSPHORUS TRIHYDRIDE, OR PHOSPHINE,  $\text{PH}_3$ .

245. **Preparation**—This gas, which is the analogue of ammonia, is obtained by heating phosphorus in a flask with a solution of caustic soda. As obtained in this way it is mixed with small quantities of the liquid and solid hydrides, which render it spontaneously inflammable in air; so, to prevent the gas taking fire in the flask, the air is, previous to heating, displaced from the apparatus by coal gas. The end of the delivery tube dips under water as shown in Fig. 61, and as each bubble of gas reaches the surface it inflames and produces a ring of white smoke (phosphorus pentoxide)

The reaction which takes place is—



Phosphine is also formed, along with a considerable quantity of liquid phosphoretted hydrogen, when phosphide of calcium (obtained by heating together lime and phosphorus in a closed crucible) is brought into contact with water.

Pure phosphorus trihydride is prepared by warming phosphonium iodide,  $\text{PH}_4\text{I}$  (see below), with caustic potash or soda, the reaction being analogous to that employed in the preparation of ammonia—

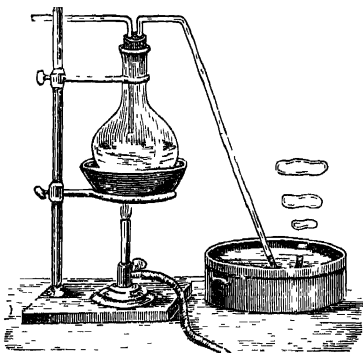
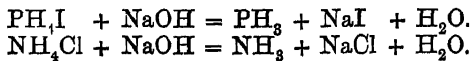


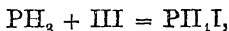
FIG. 61.



The gas may be collected over water.

246. **Properties of  $\text{PH}_3$ .**—It is a colourless gas which condenses only when cooled to  $-90^\circ \text{C}$ . It is very slightly soluble in water, and possesses a penetrating garlic-like odour which is evident even with very small quantities of the gas, it is very poisonous. If free from other hydrides, it is not inflammable in air at ordinary temperatures, heat decomposes the gas into its elements more readily than the corresponding nitrogen compound,  $\text{NH}_3$ .

Just as ammonia combines directly with the haloid acids  $\text{HCl}$ ,  $\text{HBr}$ , etc., to form ammonium chloride, ammonium bromide, etc., so phosphorus trihydride forms similar compounds. The combination with hydriodic acid to form phosphonium iodide—



takes place very readily.

#### THE OXIDES AND OXYACIDS OF PHOSPHORUS.

247. A list of the oxides and oxyacids of phosphorus which are known is given in the following table.—

Oxides.	Corresponding Acids.
$\text{P}_2\text{O}$ (not known in free state)	Hypophosphorous acid, $\text{H}_3\text{FO}_2$ or $3 \text{H}_2\text{O} \cdot \text{P}_2\text{O}$ .
$\text{P}_2\text{O}_3$ ( $\text{P}_4\text{O}_6$ )	Phosphorous acid, $\text{H}_3\text{PO}_3$ or $3 \text{H}_2\text{O} \cdot \text{P}_2\text{O}_3$
$\text{P}_2\text{O}_4$	Hypophosphoric acid, $\text{H}_4\text{P}_2\text{O}_6$ or $2 \text{H}_2\text{O} \cdot \text{P}_2\text{O}_4$
$\text{P}_2\text{O}_5$	Orthophosphoric acid, $\text{H}_3\text{PO}_4$ or $3 \text{H}_2\text{O} \cdot \text{P}_2\text{O}_5$ .
	Pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$ or $2 \text{H}_2\text{O} \cdot \text{P}_2\text{O}_5$ .
	Metaphosphoric acid, $\text{HPO}_3$ or $\text{H}_2\text{O} \cdot \text{P}_2\text{O}_5$

The more important are phosphorous oxide,  $\text{P}_4\text{O}_6$ , and phosphorus pentoxide,  $\text{P}_2\text{O}_5$ , and the acids derived from them, and we shall restrict ourselves to a study of these compounds.

PHOSPHOROUS OXIDE,  $P_4O_6$ .

•248. **Preparation.**—Phosphorous oxide is obtained mixed with phosphorus pentoxide when phosphorus is exposed to oxidation in air at ordinary temperature, or when it is burnt in a limited supply of air. Its preparation is carried out in the following manner:—

A glass tube is drawn out into the shape shown at A, Fig. 62, and some pieces of phosphorus are introduced into it. This tube is connected with a metal condenser D, the inner tube of which is provided with a plug of glass wool at the end away from A; the space between the two tubes of the condenser is filled with water. The condenser is

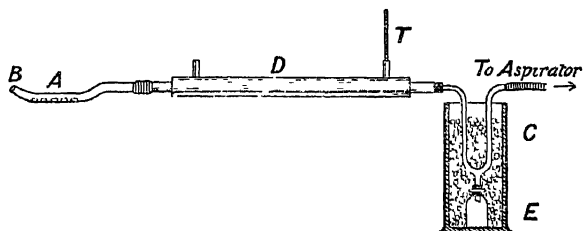
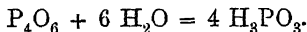


FIG. 62.

attached to a U-tube C connected at its lower end with a bottle E, as shown in the diagram; the U-tube and bottle are surrounded by a freezing mixture of ice and salt. The tube A is gently heated and a current of air is drawn through the apparatus by means of an aspirator attached to the U-tube. The phosphorus melts, but is prevented from running out by the shape of the tube; it burns in the current of air and a mixture of  $P_4O_6$  and  $P_2O_5$  passes over into D, where it condenses. After some time the condenser is heated till the temperature of the water rises to  $50^\circ C$ . as indicated by the thermometer, T. This temperature is sufficient to melt the phosphorous oxide which passes over into the U-tube, where it solidifies, but the phosphorus

pentoxide remains solid and the plug of glass wool keeps it back in D. Occasionally the freezing mixture is removed from the U-tube and bottle, and the U-tube is gently warmed, when the  $P_4O_6$  melts and runs down into bottle.

**249. Properties**—Phosphorous oxide is a white crystalline solid, melting at  $22.5^\circ \text{C}$ . to a colourless liquid. It is slowly dissolved by *cold* water with formation of phosphorous acid,  $H_3PO_3$ , and is therefore the anhydride of this acid—

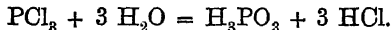


With *hot* water, however, a violent reaction takes place with formation of red phosphorus, phosphides of hydrogen and phosphoric acid. On exposure to moist air or oxygen it oxidises to phosphorus pentoxide, and if the temperature is slightly raised it takes fire.

The vapour density of phosphorous oxide is 110, and consequently its molecular weight is  $2 \times 110 = 220$ . This corresponds to a formula  $P_4O_6$  for the gaseous molecule ( $P_4 = 4 \times 31 = 124$ ,  $O_6 = 6 \times 16 = 96$ , and  $124 + 96 = 220$ ).

#### PHOSPHOROUS ACID, $H_3PO_3$

**250. Preparation.**—This acid may be obtained, as already stated, by the action of cold water on phosphorous oxide. It is prepared by the action of water on phosphorus trichloride—

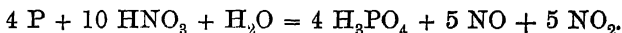


It is not necessary to actually prepare the trichloride, and the most convenient course of procedure is to pass chlorine into phosphorus melted under a layer of water. A solution of phosphorous acid is thus obtained, and on concentrating and allowing to cool, crystals of the acid separate out.

**251. Properties.**—Phosphorous acid is a white, deliquescent crystalline solid, melting at  $70^\circ \text{C}$ . Only two of the three hydrogen atoms in the molecule of phosphorous acid

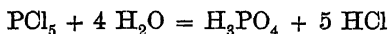


**Exp. 159**—Introduce a few pieces (say 10 grammes) of phosphorus into a large retort, and pour upon it 150 c.c. of a mixture of one part of nitric acid to two parts of water. Heat cautiously, and presently red fumes of oxides of nitrogen will be evolved by the reduction of the nitric acid—



Continue the heating in such a manner as to keep the liquid about its boiling-point, but so that as little as possible distils over. When the phosphorus has all disappeared, and red fumes are no longer generated, distil the acid over until that remaining has a syrupy consistency, more red fumes will be evolved at this stage through the oxidation of some phosphorous acid. Finally, transfer the thick liquid to a porcelain dish and evaporate so long as strongly acid fumes ( $\text{HNO}_3$ ) are given off

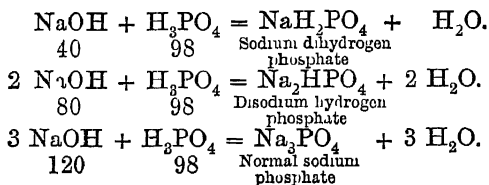
As trichloride of phosphorus when treated with excess of water yields phosphorous acid, so the pentachloride, by similar treatment, gives ordinary phosphoric acid—



The acid, when sufficiently concentrated, crystallises on standing.

**255. Properties.**—Phosphoric acid is a colourless deliquescent crystalline solid, melting at  $41.7^\circ \text{C}$ ., the crystals consist of hard rhombic prisms. It is a tribasic acid, each of the atoms of hydrogen being replaceable by a metal.

**256. The Phosphates**—The phosphates of the alkali metals sodium, potassium and of ammonium are soluble in water, and are obtained by the addition of the alkaline hydrates to phosphoric acid. The amount of the alkali added may be sufficient to replace one, two, or three atoms of the hydrogen, thus—



The numbers underneath show the combining proportions of caustic soda and phosphoric acid required to form such salts. That is to say, if to 98 grammes of phosphoric acid there be added 40 grammes of caustic soda and the solution evaporated the salt  $\text{NaH}_2\text{PO}_4$  will be obtained; if 80 grammes, then the salt formed will be  $\text{Na}_2\text{HPO}_4$ , and if 120 grammes, the salt  $\text{Na}_3\text{PO}_4$  will be formed.

$\text{Na}_3\text{PO}_4$  is an example of a *normal* salt which is *not neutral* in its reaction with litmus but *alkaline*.

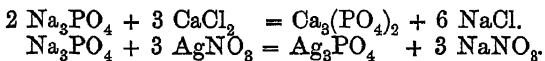
$\text{NaH}_2\text{PO}_4$ , Sodium dihydrogen phosphate—acid reaction.

$\text{Na}_2\text{HPO}_4$ , Disodium hydrogen phosphate—slightly alkaline.

$\text{Na}_3\text{PO}_4$ , Normal sodium phosphate—distinctly alkaline.

The salt ordinarily known as “sodium phosphate” is  $\text{Na}_2\text{HPO}_4$ . It is prepared by adding caustic soda solution to phosphoric acid till the liquid is distinctly alkaline and crystallising the salt. Crystals of the composition  $\text{Na}_2\text{HPO}_4 + 12 \text{H}_2\text{O}$  separate out.

The normal phosphates of the alkaline earth metals (Ba, Sr, Ca) and of Mg, Pb, Ag, and indeed of all other metals, are insoluble in water, but soluble in dilute mineral acids. They may be prepared by adding a soluble salt of the metal in question to an aqueous solution of an alkaline phosphate—



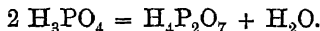
**257. Tests for Phosphates.**—(1) Ferric chloride gives, even in presence of acetic acid, a yellowish-white precipitate of ferric phosphate (Arsenates give a similar precipitate.)

(2) Silver nitrate gives a pale yellow precipitate of silver phosphate (Arsenates give a brick-red precipitate.)

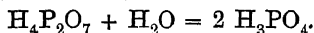
(3) Excess of ammonium molybdate in the presence of nitric acid gives a bright yellow precipitate of phosphomolybdate of ammonium even in the cold, but more rapidly on warming. (The arsenates give a similar precipitate only on warming.)

(4) The presence of phosphorus may always be detected by heating a little of the powdered substance along with magnesium filings in a narrow tube and then moistening the product with water. Phosphoretted hydrogen is given off, and may be recognised by its characteristic odour.

258. **Pyrophosphoric Acid**,  $\text{H}_4\text{P}_2\text{O}_7$ , is obtained as a glassy mass by heating ordinary phosphoric acid to  $215^\circ \text{C}$ .—



It is readily soluble in water and in solution is slowly converted into orthophosphoric acid at the ordinary temperature, rapidly on boiling—



As with the phosphates, the salts of the alkali metals are soluble in water, those of the other metals being insoluble in water but soluble in dilute mineral acids.

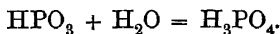
**Tests for Pyrophosphates.**—(1) Silver nitrate gives a *white* precipitate of  $\text{Ag}_4\text{P}_2\text{O}_7$  (distinction from phosphates).

(2) Pyrophosphoric acid does not coagulate albumen (distinction from metaphosphoric acid)

259. **Metaphosphoric Acid**,  $\text{HPO}_3$ , is obtained when ortho- or pyrophosphoric acid or their ammonium salts are strongly heated—



It is a glassy solid (whence the name *glacial phosphoric acid* by which it is also known) and closely resembles pyrophosphoric acid in appearance. It is readily soluble in water, and in solution passes slowly into orthophosphoric acid; on heating the change takes place rapidly—



The salts of  $\text{HPO}_3$  resemble those of  $\text{H}_3\text{PO}_4$  and  $\text{H}_4\text{P}_2\text{O}_7$  as regards their solubility in water and acids.

**Tests for Metaphosphates.**—(1) Silver nitrate gives *white* precipitate of  $\text{AgPO}_3$  (distinction for phosphates).

(2) Metaphosphoric acid coagulates albumen (distinction from ortho- and pyrophosphoric acids)

### COMPOUNDS OF PHOSPHORUS WITH THE HALOGENS.

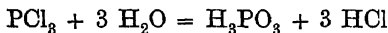
260. By direct union of phosphorus with these elements, bodies of the type  $\text{PX}_3$  and  $\text{PX}_5$  are formed, and by the action of moisture on  $\text{PCl}_5$  and  $\text{PBr}_5$ , the oxychloride  $\text{POCl}_3$ , and oxybromide  $\text{POBr}_3$ , respectively, are obtained.

We shall only consider the compounds  $\text{PCl}_3$  and  $\text{PCl}_5$  in detail; the corresponding compounds of the other halogens closely resemble them in properties.

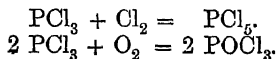
### PHOSPHORUS TRICHLORIDE, $\text{PCl}_3$

261 **Preparation**—This compound is prepared by passing dry chlorine over red phosphorus heated in a glass retort, the trichloride distils over and is collected in a receiver cooled by water

**Properties.**—Phosphorus trichloride is a colourless mobile liquid boiling at  $76^\circ \text{C}$ . It is decomposed by water with formation of phosphorous and hydrochloric acids—



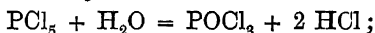
It combines directly with chlorine to form phosphorus pentachloride, and on heating unites with oxygen, forming phosphorus oxychloride,  $\text{POCl}_3$ —



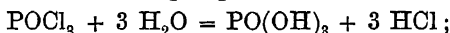
PHOSPHORUS PENTACHLORIDE,  $\text{PCl}_5$ .

262. **Preparation**—Phosphorus pentachloride is prepared by passing chlorine into phosphorus trichloride contained in a flask, using a wide delivery tube, so that the end will not be stopped up by the solid pentachloride

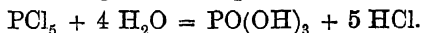
**Properties**—The pentachloride is a light yellow solid, which passes directly into vapour at  $168^\circ \text{C.}$ , without melting, undergoing partial decomposition into  $\text{PCl}_3$  and  $\text{Cl}_2$ . With a small quantity of water phosphorus pentachloride yields phosphorus oxychloride—



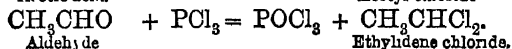
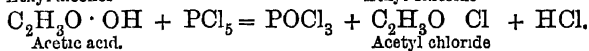
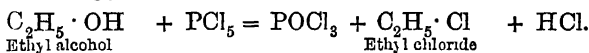
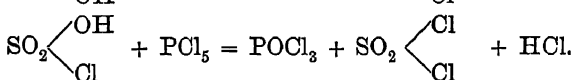
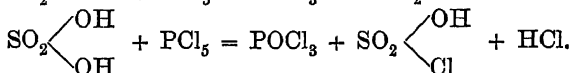
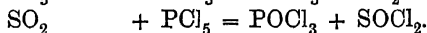
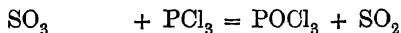
but with excess of water phosphoric acid is formed—



or, writing both stages in one equation—



The greater attraction which phosphorus has for oxygen than for chlorine renders both  $\text{PCl}_3$  and  $\text{PCl}_5$  valuable reagents for substituting chlorine for oxygen or hydroxyl, in the latter case with elimination of  $\text{HCl}$ , they are much used for this purpose in dealing with carbon compounds. Examples of such actions are given in the following equations:



## QUESTIONS — CHAPTER XX.

1. What is the effect of heating chlorapatite and fluorapatite respectively with concentrated sulphuric acid?
2. How is phosphorus extracted from phosphoric acid?
3. Discuss the nature of the changes which take place when phosphorus undergoes slow oxidation in air.
4. Write down in parallel columns the physical properties of ordinary and red phosphorus.
5. What differences are there in chemical behaviour between ordinary and red phosphorus?
6. Why does a match ignite when rubbed on a rough surface? What chemical action takes place during the ignition?
7. To what is the spontaneous ignition of phosphorus trihydride due, and how may the hydride be prepared so as not to ignite spontaneously?
8. Express by equations the action of phosphorus on chlorine, iodine, caustic potash and nitric acid.
9. Compare the trihydride of phosphorus with the trihydride of nitrogen.
10. How is phosphorous oxide prepared, and how may it be converted into the pentoxide?
11. What is the action of (a) cold water, (b) hot water on phosphorous oxide?
12. How has it been proved that the formula for phosphorous oxide is  $P_4O_6$ , not  $P_2O_3$ ?
13. Describe the preparation and properties of phosphorous acid.
14. How may phosphorus pentoxide be obtained in quantity and converted into metaphosphoric acid and into phosphoric acid?
15. What is the action of water on the trichloride and on the pentachloride of phosphorus? Give equations.
16. Describe in detail the preparation of phosphoric acid from phosphorus.

- 17 What is meant by saying that orthophosphoric acid is a *tribasic* acid? Write down the names and formulæ of a few phosphates that are soluble in water
18. By what chemical tests may phosphates be distinguished from arsenates and from pyrophosphates?
- 19 How are metaphosphoric and pyrophosphoric acids prepared and distinguished?
- 20 Describe the preparation of the chlorides of phosphorus and of phosphorus oxychloride.
21. 50 grammes of caustic soda are mixed with 61.25 grammes of orthophosphoric acid. What salt will be produced and how much of it will be obtained?

(Na = 23, O = 16, H = 1, P = 31.)

## CHAPTER XXI.

### CARBON AND THE HYDROCARBONS.

#### CARBON.

263 CARBON is the first member of a group consisting of the elements carbon, silicon, titanium, zirconium, and thorium, of which the first two members alone come under consideration amongst the non-metals. They show a considerable resemblance to one another in their physical and chemical properties.

Comparing together more particularly carbon and silicon we observe that—

- (1) The elements themselves are very infusible
- (2) They exist in allotropic modifications of similar character
- (3) They form oxides of great stability and also gaseous hydrides,  $\text{CH}_4$  and  $\text{SiH}_4$ , the former of these being a stable body, whilst the latter undergoes decomposition very readily.
- (4) Carbon and silicon both combine directly with fluorine to form  $\text{CF}_4$  and  $\text{SiF}_4$  respectively. With the other halogen elements they do not combine directly, but volatile liquid tetrachlorides,  $\text{CCl}_4$  and  $\text{SiCl}_4$ , are obtained indirectly.

264. Occurrence.—Carbon is found in nature in a state of comparative purity as diamond and graphite, the latter known as mineral plumbago, from which black-lead pencils



are made. These forms do not, however, occur in any very considerable quantity, and the sources from which the large supplies of carbon are obtained are coal and vegetable matter.

The tissue of plants is very constant in composition, and disregarding the moisture and the mineral ash left after combustion, amounting usually to about 1 per cent., *dried wood* is found to consist of

Carbon	...	...	...	50 per cent.
Hydrogen	...	.	..	6 "
Oxygen and nitrogen	...	..		44 "

Where plants undergo decay and form thick accumulations of *peat*, the relative proportion of the carbon increases, and the following may be taken as the average composition of peat, leaving out of account moisture and mineral matter—

Carbon	...	...	...	58 per cent.
Hydrogen	...	...	..	5 "
Oxygen and nitrogen	...	...		37 "

In deposits of peat and the remains of vegetation which have lain for long periods of time this process of parting with the more volatile constituents and consequent increase in the proportion of carbon goes on, and instead of peat we have a much denser product known as *brown coal* or *lignite*, in which the structure of the vegetation composing it can, however, still be observed. Lignite varies greatly in composition, especially in regard to the amount of moisture and ash. Excluding these, it contains on the average—

Carbon	...	...	...	66 per cent.
Hydrogen	...	..	..	5 "
Oxygen and nitrogen		..		29 "

In the older formations of the earth's crust there are large deposits of *coal*, which have resulted from long-continued action similar to the foregoing. The seams of

coal usually occur at some depth, and are overlaid by other strata. The vegetable tissue from which coal is derived has thus been subjected to immense pressure and to increased temperature, and under these agencies, acting over long periods of time, the changes already noticed in the passage from woody tissue to lignite have been still further accentuated. Coal is darker in colour, denser, and more brittle, as to composition, the following numbers may be compared with those given for wood, peat, and lignite—

	Bituminous coal	Anthracite.
Carbon . . . . .	84 per cent.	94 per cent.
Hydrogen .. .. .	5 „	3 „
Oxygen and nitrogen ...	11 „	3 „

Over 200 million tons of coal are brought to the surface in the United Kingdom annually.

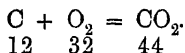
In many localities, especially in South Russia and the United States, there are large deposits of *petroleum*—a mixture of various oils, but all composed of carbon and hydrogen, and hence termed hydrocarbons.

And when we add the very extensive series of carbon compounds which have been prepared in the laboratory from coal and petroleum, and the products, such as starch, sugar, turpentine, albumen, stearin, etc., elaborated by plants and animals, we are in a position to appreciate the immense importance of the element carbon. The study of such bodies is indeed set apart as a special branch of the science, and known as *Organic Chemistry*, or the *Chemistry of the Carbon Compounds*.

Finally, carbon occurs in combination with oxygen as carbon dioxide in the air, and in vast deposits of limestone and dolomite. The carbon dioxide in air, being less than 4 volumes in 10,000, might be regarded as insignificant, but the mass of the atmosphere is such that at this computation there must be very nearly a billion tons of carbon in it.

265 Allotropic Forms of Carbon —(1) *Diamond* is a crystalline form of carbon, it is found in South Africa and Brazil, usually as octahedra or cubes, or as some modifications of these. Its value is due to its great hardness and brilliancy of lustre, and to the fact that it does not oxidise or undergo change even in presence of corrosive substances. It is the densest form of carbon, having a specific gravity of about 3·5, and is also the most difficult to ignite in oxygen.

It is therefore not to be wondered at that the composition of diamond remained unknown until the time of Lavoisier, although it had been previously observed that diamond could be burnt and left no appreciable residue. Lavoisier about a century ago, by means of a burning glass, ignited diamond in air enclosed over mercury, and found that when it burnt, the gas which was formed turned lime-water milky and was carbon dioxide. Dumas, later, showed that carbon dioxide was the *only product* obtained when diamond is burnt in oxygen, and that every 12 parts by weight of diamond yielded 44 parts of carbon dioxide, according to the equation—



Diamond consists, therefore (with the exception of a minute quantity of ash), of pure carbon.

Moissan has recently succeeded in preparing small diamonds artificially from charcoal by means of the electric furnace. Iron and carbon are placed in a crucible which is then introduced into an electric furnace and raised to a high temperature. The iron melts and dissolves the carbon; on now placing the crucible in a bath of molten lead the outer layer of iron solidifies, contracts, and in so doing exerts great pressure on the still liquid metal inside. Under these conditions some of the carbon crystallises out in the form of diamond. The iron is dissolved in hydrochloric acid, and the residue is found to contain small diamonds, some of which are colourless, others are

black (called *carbonado*). A portion of the residue is also in the form of graphite

(2) *Graphite*—This also occurs naturally, being found usually in the older crystalline rocks. Cast-iron contains plates of this form of carbon, which can be seen at a freshly-fractured surface, and masses of it accumulate at the base of blast furnaces. It is a soft, dark-grey substance, with an almost metallic lustre, and possesses a much lower specific gravity (2.2) than diamond.

It is usually found massive, but occasionally in six-sided crystals. When rubbed on paper it leaves a black mark, and is therefore used in making lead pencils. It is (unlike diamond) a good conductor of heat and electricity, and on the latter account is used in electrotyping. Graphite is very infusible, and on this account is largely used in the manufacture of "plumbago" crucibles. It is also used as a lubricant for machinery and for polishing gunpowder. When strongly heated in oxygen graphite burns with formation of carbon dioxide; the ash which is left consists of silica, ferric oxide, and alumina. Graphite is oxidised when gently heated with a mixture of  $\text{KClO}_3$  and  $\text{HNO}_3$ , whilst diamond is unattacked.

*Artificial graphite* is now manufactured by heating charcoal or coke with excess of iron in the electric furnace.

(3) *Amorphous carbon* is familiar to us as charcoal, lamp-black, or animal charcoal, which, however, are usually more or less impure forms of carbon.

266 **Charcoal** may be obtained by strongly heating wood or many other organic bodies in vessels from which air is excluded; or by the action of dehydrating substances, such as strong sulphuric acid, on these bodies.

**Exp. 160**—Heat a few pieces of wood in a hard glass tube over the flame of a Bunsen burner. Volatile vapours are at first given off and burn at the mouth of the tube; when these are no longer to be seen, throw out the contents of the tube into water. The black charred product is wood charcoal.

**Exp. 161**.—Make about 100 grammes of sugar into a thick syrup by dissolving it in a small quantity of hot water, and place it in a deep glass cylinder; then pour in about 100 c.c. of concentrated

**sulphuric acid** Presently the liquid will blacken and froth considerably, and a mass of black charcoal much more bulky than the sugar originally taken will be formed. Wash this thoroughly with water till free from acid, and there remains carbon in a granular condition.

Where wood is scarce, charcoal is prepared from it by distillation, as already mentioned, but where it is plentiful and waste is not important, the logs are arranged in heaps, covered with sods or earth to allow only a small supply of air, and then slowly burned.

**267. Properties of Charcoal.**—The chemical composition and properties of charcoal vary considerably with the kind of wood used and the temperature at which it is charred. When charred at a low temperature the charcoal is soft and light in colour, and it burns easily; it also contains a lower percentage of carbon than when charred at a high temperature. Thus a specimen of wood charred at a temperature of about  $300^{\circ}\text{C}$  contained 70 per cent of carbon and 4.5 per cent of hydrogen, while when charred at a full white heat it contained 96 per cent of carbon and 0.5 per cent. of hydrogen.

Wood charcoal has a specific gravity of about 1.5; yet when dry it floats on water. This is explained when a piece of charcoal is placed on water under the receiver of an air pump: as the pump is worked, air escapes from the charcoal and it gradually sinks. The charcoal is porous, and the air contained in its pores reduces its apparent specific gravity to about 0.2, the specific gravity of air being only about 0.0013 (water = 1).

Charcoal also absorbs other gases to a varying extent.

Cocoa-nut charcoal, under favourable conditions, was found to absorb of—

Ammonia	...	..	172	times its volume.
Hydrochloric acid	...	165	”	”
Nitrous oxide	...	99	”	”
Carbon dioxide	...	97	”	”

On the other hand, charcoal only absorbs slightly more than its own volume of hydrogen.

**Exp 162**—Fill a test-tube with dry ammonia gas by displacement, and stand it over mercury in a trough. Heat a small piece of charcoal red hot in the crucible tongs, and plunge it, while still glowing, under the mercury, then allow it to rise into the test-tube. The mercury rises in the tube as the ammonia is rapidly absorbed by the charcoal.

This property of charcoal is used in deodorising and disinfecting sewers and hospital wards. The charcoal not only absorbs gases and the effluvia evolved by putrefying matter, but also rapidly oxidises them by means of the oxygen already present in its pores: this oxygen is more active than ordinary gaseous oxygen, and is even capable of killing bacteria.

**Exp. 163**—Mix a little finely-powdered wood charcoal with water, and pour the whole on to a filter paper in a funnel. Pour some sulphuretted hydrogen water through the charcoal and test the filtrate by lead acetate solution. No black precipitate of lead sulphide is formed, showing that the sulphuretted hydrogen has been oxidised by the oxygen absorbed in the charcoal.

Charcoal also possesses the power of decolorising liquids; for this purpose animal charcoal is more generally used (see § 270).

Charcoal burns in air without flame or smoke, unless it has been prepared at a low temperature and is therefore very impure, in excess of air carbon dioxide ( $\text{CO}_2$ ) is produced, but in a limited supply of air carbon monoxide ( $\text{CO}$ ) is formed.

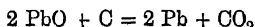
**268. Reducing action of Charcoal.**—On account of the ease with which it combines with oxygen, charcoal (and other forms of amorphous carbon) acts as a strong reducing agent at high temperatures.

We have already had an example of a *gaseous* reducing agent in hydrogen, which, owing to its affinity for oxygen, reduces many oxides to the metallic condition. Also in sulphurous acid or phosphorous acid we have instances of *liquids* as reducing agents, their activity being due to the ease with which they undergo oxidation to sulphuric acid and phosphoric acid respectively. In carbon we have a

*solid* reducing agent which finds very frequent employment in operations conducted at high temperatures, the carbon under such conditions being oxidised to carbon monoxide or dioxide at the expense of the oxygen contained in the bodies with which it is mixed

Thus, most metallurgical operations involving a reduction of oxides to the metal are carried out with the use of carbon in the form of coke or coal, which is oxidised to CO or CO<sub>2</sub> in the process

**Exp. 164.**—Make an intimate mixture of about a gramme of finely-powdered oxide of lead (litharge) with about one-tenth its weight of charcoal, and heat to redness in a hard glass tube or porcelain crucible for five minutes. Now throw some of the powder into a mortar with a little water and rub it up, using pressure, with the pestle, and then wash away the charcoal by means of a stream of water. Pellets or plates of metallic lead will be obtained—



Similarly, oxide of copper or bismuth may be reduced, and metallic copper or bismuth obtained from them. The reduction of iron ores, or oxide of zinc or tin, are examples of similar reductions carried out on the large scale

**269. Preparation of pure Charcoal.**—*Pure* charcoal may be prepared by dehydrating pure cane-sugar as in Exp. 161, and then heating it in a current of chlorine, when any hydrogen present is removed as hydrochloric acid. An alternative method is to heat the cane-sugar in a platinum crucible when water is driven off, the product is then treated with chlorine as before.

**270. Animal Charcoal, or Bone Black.**—Another kind of charcoal is made by heating bones in closed iron retorts. It is a very porous mixture of charcoal with the mineral constituents of the bones, chiefly calcium phosphate. It is used for decolorising raw sugar, as it has the property already referred to of removing many colouring matters from solution.

**Exp. 165** —Shake up with animal charcoal a hot solution of indigo or litmus for a few moments and then pour it on a filter, the filtrate will be colourless. That the colouring matter is removed by the animal charcoal and not by the filter, may be shown by pouring a similar solution, which has not been treated by animal charcoal, through a filter paper.

**271. Lamp-black** may be made by burning resin or turpentine, and bringing a cool surface, *e.g.* the under-side of a porcelain basin filled with cold water, into the flame. In this form, after treatment with chlorine, a particularly pure and finely-divided form of carbon is prepared.

Lamp-black is used in making paint and printers' ink.

**272. Gas-carbon and Coke** —Two forms of amorphous carbon are obtained by the destructive distillation\* of coal (see §§ 285, 286), namely, *gas-carbon* and *coke*. The former is nearly pure carbon, but the latter contains all the non-volatile products present in the coal. Gas-carbon is very hard and has a specific gravity of 2.35. It is a good conductor of electricity, and is on this account used for making the carbon electrodes of arc lights.

**273** In whatever form it occurs, carbon is infusible, but it volatilizes without fusion at the temperature of the electric furnace. It cannot be considered an element of great chemical activity, since at ordinary or moderate temperatures it does not combine directly with any of the elements except fluorine. At high temperatures, however, carbon does unite directly with a considerable number of elements, *e.g.* oxygen, sulphur, hydrogen, nitrogen, iron and aluminium.

**274. Proof that the Allotropic Modifications of Carbon all consist of the Same Element** —The best proof consists in showing that whichever allotropic modification is used, 12 parts by weight of it on combustion in oxygen yield 44 parts by weight of carbon dioxide. We have already seen in § 265 that Dumas adopted this method in the case of diamond. The experiment may be carried out in the

\* The process of *destructive distillation* consists in distilling a complex substance, such as wood or coal, out of contact with air.



following manner:—A small quantity of any form of carbon (say graphite) is accurately weighed out in a porcelain "boat" C (Fig 64); this is then introduced into one end of a hard glass tube, the greater part of which is filled with granulated copper oxide. The tube is closed at each end with a one-holed rubber cork through which passes a short glass tube. The end of the tube at which the boat is placed is connected with a supply of dry oxygen, the other end with a series of bulbs containing strong caustic potash solution. These bulbs, together with a calcium chloride tube A (the object of which is explained in § 213, where a similar experiment is described with sulphur), are weighed, before being placed in position. The tube is now heated in a furnace; at first only the burners under the copper oxide are lighted, but when this becomes red-hot the heating is extended to the boat and a slow

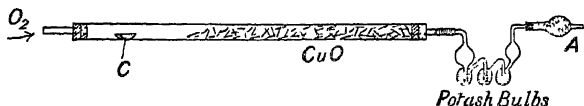


FIG 64.

current of oxygen is passed through the tube. The carbon burns to carbon dioxide, which passes on and is absorbed by the caustic potash. Any carbon monoxide which is at first formed owing to incomplete combustion is converted into carbon dioxide during its passage over the heated copper oxide. When nothing remains in the boat but a trace of ash, and when bubbles of gas cease to be absorbed in the potash bulbs, the latter are disconnected and after cooling are reweighed (together with the calcium chloride tube). The increase in weight gives the weight of carbon dioxide formed. The boat is also allowed to cool and is reweighed. The difference between the final weight of the boat (which includes the weight of the ash) and the weight of the boat + graphite (previously determined) gives the actual weight of graphite burnt (*i.e.* the ash is allowed for).

Let  $W_1$  = weight of boat + graphite.

$W_2$  = weight of boat + ash.

Then  $W_1 - W_2$  = weight of graphite burnt.

Also let  $W_3$  = weight of KOH bulbs + CaCl<sub>2</sub> tube  
before absorption,

and  $W_4$  = weight of KOH bulbs + CaCl<sub>2</sub> tube  
after absorption,

Then  $W_4 - W_3$  = weight of CO<sub>2</sub> formed.

It will then be found that whatever form of carbon is used the ratio  $\frac{W_4 - W_3}{W_1 - W_2}$  is equal to  $\frac{44}{12}$  or  $\frac{11}{3}$ .

### HYDROCARBONS.

275. These are compounds consisting of carbon and hydrogen alone. The direct combination of carbon and hydrogen in the laboratory can only be effected with difficulty (marsh gas, CH<sub>4</sub>, and acetylene, C<sub>2</sub>H<sub>2</sub>, being formed), and yet the number of known hydrocarbons is exceedingly great.

They vary in physical and chemical character according to their composition, and according to the arrangement of the ultimate particles of carbon and hydrogen of which they are composed. Hydrocarbons containing a small number of atoms of carbon and hydrogen are usually gaseous, such as marsh gas, CH<sub>4</sub>, ethylene or olefiant gas, C<sub>2</sub>H<sub>4</sub>, acetylene, C<sub>2</sub>H<sub>2</sub>, and those whose composition is more complex are at ordinary temperatures liquid, such as pentane, C<sub>5</sub>H<sub>12</sub>, benzene, C<sub>6</sub>H<sub>6</sub>, oil of turpentine, C<sub>10</sub>H<sub>16</sub>; or solid, such as naphthalene, C<sub>10</sub>H<sub>8</sub>, anthracene, C<sub>14</sub>H<sub>10</sub>.

The hydrocarbons may be arranged in series in accordance with the relative numbers of atoms of carbon and hydrogen which they contain—

(1) The *Marsh Gas Series* (or Paraffins), the first member of which is marsh gas, CH<sub>4</sub>, and succeeding members, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and so on, the general expression for the relation of carbon to hydrogen being C<sub>n</sub>H<sub>2n+2</sub>.

(2) The *Ethylene Series* (or Olefines), the first member of which is ethylene,  $C_2H_4$ , and succeeding members,  $C_3H_6$ ,  $C_4H_8$ , and so on, the general expression for the relation of carbon to hydrogen being  $C_nH_{2n}$ .

(3) The *Acetylene Series*, the first member of which is acetylene,  $C_2H_2$ , and succeeding members,  $C_3H_4$ ,  $C_4H_6$ , and so on, the general expression for the relation of carbon to hydrogen being  $C_nH_{2n-2}$ .

(4) Hydrocarbons having the general formula  $C_nH_{2n-4}$  and  $C_nH_{2n-6}$ , and others having still smaller proportions of hydrogen, are known, a familiar example of the  $C_nH_{2n-6}$  series being benzene,  $C_6H_6$ , the first member of this series.

At this stage we shall only take into consideration the three hydrocarbons, marsh gas, ethylene, and acetylene.

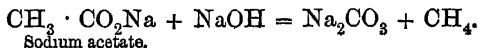
#### MARSH GAS OR METHANE, $CH_4$ .

**276. Occurrence.**—This gas is so called because it is frequently generated in marshes or pools where vegetable matter is in course of decay. The “blowers” in coal-mines discharge large quantities of this gas, which from its inflammable nature is termed “fire-damp,” and it is also formed in the destructive distillation of wood or coal, coal gas containing usually about 35 per cent of marsh gas.

**277. Preparation.**—When charcoal is heated in an atmosphere of hydrogen to a temperature of  $1,200^\circ C$  a certain amount of chemical combination takes place, with formation of marsh gas

It is also produced, together with acetylene, when electric sparks are passed between carbon poles in an atmosphere of hydrogen

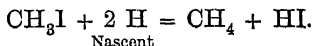
Marsh gas is prepared by strongly heating a mixture of anhydrous sodium acetate and dry soda-lime (lime which has been slaked by the addition of caustic soda solution)—



**Exp 166.**—Weigh out about 10 grammes of anhydrous sodium acetate and 30 grammes of soda-lime; intimately mix them in a mortar and dry by gently heating in a porcelain dish. Introduce the mixture into a small hard glass flask provided with a cork and delivery tube, and heat strongly. Collect the gas which is evolved over water at the pneumatic trough.

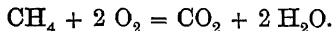
As thus prepared marsh gas is by no means pure; it is contaminated with ethylene,  $C_2H_4$ , and hydrogen. The former may be removed to a large extent by passing the gas through a wash-bottle containing strong sulphuric acid.

Pure marsh gas may be obtained by the action of nascent hydrogen on methyl iodide,  $CH_3I$ .



The methyl iodide is dissolved in a mixture of alcohol and water and zinc-copper couple added. The two last react with formation of hydrogen which then reduces the methyl iodide. The presence of alcohol is necessary because methyl iodide is insoluble in pure water.

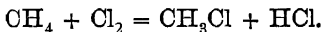
**278. Properties.**—Marsh gas or methane is a colourless and odourless gas, which at  $0^\circ C$ . is condensed to the liquid form under a pressure of 140 atmospheres. It is only slightly soluble in water, 100 volumes of which at  $0^\circ C$ . dissolve 5.5 volumes of the gas. It burns with a pale blue non-luminous flame, forming carbon dioxide and water vapour—



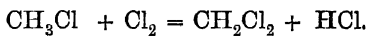
With oxygen or air within certain limits it forms an explosive mixture, and the explosions occurring in coal-mines are usually due to the firing of such a mixture. With the halogen elements\* it forms compounds in which part or even the whole of the hydrogen is replaced atom

\* *Iodine* does not act directly on marsh gas except in the presence of a substance such as iodic acid, which destroys the HI as soon as it is formed, and so prevents it from exercising a reducing action on the substitution product formed, with re-formation of  $CH_4$ .

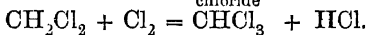
for atom by these elements, this process is known as *substitution*, and the compounds produced are called *substitution products* as already mentioned in § 134. Thus when equal volumes of chlorine and marsh gas are mixed in *diffused daylight*, they gradually react with formation of methyl chloride,  $\text{CH}_3\text{Cl}$ , and hydrochloric acid—



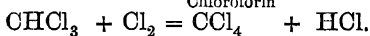
If more chlorine is present it gradually replaces the remaining hydrogen till finally the whole of the hydrogen is removed. The equations expressing the reactions which take place are as follows—



Methylene  
chloride

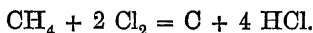


Chloroform



Carbon  
tetrachloride.

On mixing chlorine and marsh gas in direct sunlight an explosion occurs with separation of carbon—



**279. Composition of Marsh Gas.**—This may be determined by exploding a known volume (say 30 c.c.) with an excess of oxygen (120 c.c.) in a eudiometer; the carbon and hydrogen unite with oxygen to form carbon dioxide and water vapour respectively. No diminution in volume will occur if the experiment be performed at  $100^\circ \text{C}$ , that is, so long as the water remains in the form of vapour; but when the water condenses, a diminution of 60 c.c. will be recorded. Carbon dioxide and the excess of oxygen remain, and the amount of the former may be found by absorbing it with caustic potash, this will give a reduction of 30 c.c., the oxygen excess being 60 c.c. Expressing this shortly we have—

2 vols. marsh gas + 8 vols. oxygen = 4 vols. water  
vapour + 2 vols. carbon dioxide + 4 vols. oxygen

Now water vapour contains its own volume of hydrogen, and two volumes of marsh gas therefore consist of four volumes of hydrogen, and that amount of carbon which is contained in two volumes of carbon dioxide, *i.e.* one atom. This would give us the composition  $\text{CH}_4$ .

We find, by weighing, that the density of marsh gas as compared with hydrogen is 8, so that its molecular weight must be 16: this agrees with the formula  $\text{CH}_4$ , for  $\text{C} = 12$ ,  $\text{H}_4 = 4 \times 1$ , and  $12 + 4 = 16$ .

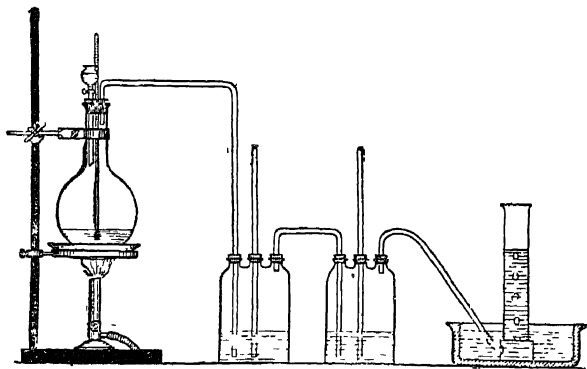
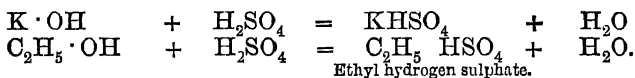


Fig. 65.

### ETHYLENE OR OLEFIANT GAS, $\text{C}_2\text{H}_4$ .

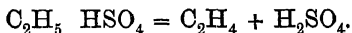
280. This gas occurs as one of the products of the destructive distillation of coal, and the luminosity of the coal gas flame is largely owing to its presence.

**Preparation.**—Ethylene is prepared by heating a mixture of alcohol,  $\text{C}_2\text{H}_5\text{OH}$ , and excess of sulphuric acid. Alcohol behaves towards sulphuric acid just like caustic potash does, *i.e.* it forms a salt with elimination of water—



The group of elements  $\text{C}_2\text{H}_5$  is called ethyl, and plays the part of a metal.

When ethyl hydrogen sulphate is heated, however, it decomposes with formation of ethylene and sulphuric acid—



The last two equations represent, therefore, the two stages of the reaction which takes place in the preparation of ethylene.

**Exp. 167.**—Mix together 200 c.c. of sulphuric acid and 50 c.c. of water, and cautiously add 50 c.c. of alcohol. Pour into a wide-mouthed flask of about a litre capacity, fitted with a cork through which pass (1) a rather wide delivery tube, (2) a thermometer, (3) a tap funnel (see Fig 65) Heat the liquid on a sand-bath until the temperature rises to  $165^\circ \text{C}$ . and keep as near this as possible. If the alcohol is impure a good deal of frothing occurs, which is, however, less troublesome if sand has been introduced into the flask. The gas should be passed through wash-bottles containing a solution of caustic soda to absorb carbon dioxide and sulphur dioxide, and collected over water, but the first three or four cylinders of it should be rejected, as they contain a very explosive mixture of ethylene and the air displaced from the flask and wash-bottles.

Syrupy phosphoric acid of such a concentration that it boils at  $200^\circ \text{C}$ . may with advantage be substituted for sulphuric acid. When this is used the frothing and charring are avoided, and,  $\text{CO}_2$  and  $\text{SO}_2$  being absent, the washing of the gas may be dispensed with.

**281 Properties**—Ethylene is a colourless gas which is freely soluble in alcohol, but only slightly soluble in water, 100 volumes of water dissolving about 25.6 volumes of the gas at  $0^\circ \text{C}$ . It is more easily condensed to the liquid form than marsh gas, requiring a pressure of

43 atmospheres at  $0^{\circ}$  C.; the liquid boils at  $-103^{\circ}$  C. under normal pressure. The gas burns with a luminous flame, which is smoky unless it is diluted with hydrogen or marsh gas. It combines directly with chlorine to form an oily liquid,  $C_2H_4Cl_2$ , hence the name *olefiant* gas.

One molecule of ethylene also combines directly with one molecule of each of the following—bromine, iodine, hydrobromic acid, hydriodic acid, sulphuric acid, and with two atoms of nascent hydrogen. On account of this property of forming *addition* compounds ethylene is said to be *unsaturated*, marsh gas, which only forms *substitution* compounds, is said to be *saturated*.

With oxygen ethylene explodes on ignition much more powerfully than marsh gas, and great care must be exercised in dealing with mixtures of ethylene with air or oxygen.

The composition of ethylene is established by a similar method to that employed in the case of marsh gas.

### ACETYLENE, $C_2H_2$ .

282 This gas occurs in small quantity in coal gas, and is formed when coal gas is burnt with an insufficient supply of air, or when the flame is cooled by impinging on a cold surface. Carbon and hydrogen unite directly to form acetylene when a powerful electric discharge is passed between carbon poles in an atmosphere of hydrogen.

**Preparation.**—One method of preparation is described in the following experiment—

Exp 168—Fit into an ordinary lamp-chimney a cork through which passes a short piece of straight wide tubing, and a second narrow piece bent at right angles, as shown in Fig. 66, and connected with the supply of coal gas. Close the aperture at the top of the chimney, and allow the gas to escape by the straight tube until the air is displaced; then light it at the lower extremity of this tube and uncover the aperture at the top of the chimney. The flame will then pass up the tube and attach itself to the inner opening where the air and coal gas meet, the flame area being air and the surrounding atmosphere being coal gas. The gas



escaping at the top of the chimney may be ignited, and here we shall have a flame of coal gas burning in air as in combustion under ordinary circumstances. In the flame burning in coal gas at the base of the chimney much acetylene is formed, and if a glass tube be passed through the upper flame and gas be aspirated from the inside of the lamp glass it will be found to contain acetylene. An ammoniacal solution of cuprous chloride absorbs acetylene with the formation of a brown powder, cuprous acetylide,  $\text{Cu}_2\text{C}_2$ , a body which in the dry condition detonates violently by friction or if heated. If this body be prepared by aspirating the gas as above through such a solution, then pure acetylene may be liberated from the moist cuprous acetylide by acting on it with hydrochloric acid—

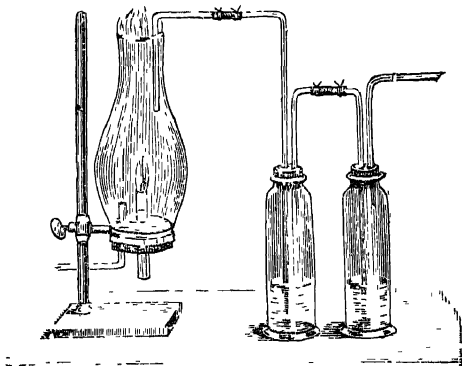
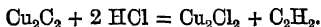
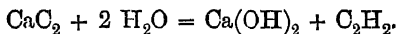


FIG. 66

The most convenient mode of preparation consists in treating calcium carbide,  $\text{CaC}_2$  (a grey solid obtained by heating lime or limestone and coke in an electric furnace), with water—



**Exp 169** — Place a small lump of calcium carbide under a cylinder of water inverted in a trough of water. Acetylene is formed without heating and rises up into the cylinder.

283. Properties — Acetylene is a colourless gas which possesses an odour of garlic (*not* the odour observed when a Bunsen lamp burns at the base), it is poisonous.

Water dissolves its own volume of the gas at ordinary temperatures, and it may be condensed to a liquid under a pressure of 48 atmospheres. It burns with a luminous smoky flame, and forms very explosive mixtures with air or oxygen.

By using a burner with a very fine hole, the flame of acetylene becomes non-smoky and exceedingly luminous. As might be expected, the gas is employed to a considerable extent for illuminating purposes, *e g.* in bicycle lamps, and, more recently, for house illumination where coal gas is not available; it is generated as required by the action of water on calcium carbide, for it cannot safely be stored under pressure on account of its tendency to explode when compressed. Acetylene is also used to increase the luminosity of other gases, such as oil gas.

Acetylene combines *directly* with either *one* or *two* molecules of chlorine or bromine; it is therefore more unsaturated than ethylene, which can only take up *one* molecule of each of these elements. It also combines directly with the halogen acids and with nascent hydrogen.

### COAL GAS AND WOOD GAS.

284. Before dealing with the manufacture of coal gas on the large scale it will be well to examine the action of heat on coal by experiment.

#### Action of Heat on Coal —

Exp. 170.—Examine a coal fire, or heat a small piece of coal in a gas flame. You will notice the softening of the coal where it is heated, the giving off of an inflammable gas, and the final burning of the coal. The coal also lights easily.

Exp. 171 —Take a jar of oxygen and lower into it a small piece of coal on a deflagrating spoon after lighting a corner. When the coal has stopped burning, test the contents of the jar for water by means of anhydrous copper sulphate and for carbon dioxide by lime water.

The products of combustion are thus seen to be carbon dioxide and steam

• **Exp 172** —Set up the apparatus shown in Fig 67. A is a hard glass tube about 6 inches long. B is a wide test-tube. Before placing A in position half-fill it with dry coal dust and shake to make an air space over the coal dust. Heat the tube carefully. Note the formation of smoke and brown fumes which condense to a liquid in B. This liquid separates out into two layers, the upper layer is an aqueous solution of various substances—*gas liquor*, the thick brown lower layer is *tar*. After some time apply a light to the gas escaping at C; it burns: this inflammable gas is *coal gas*. Test the gas with lead acetate paper; note the blackening, showing the presence of *sulphur* compounds in the gas. When the gas has stopped coming off break the tube A and note the hard *coke*.

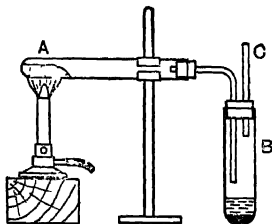



FIG 67.

285. **Manufacture of Coal Gas.**—This experiment is repeated on the large scale in the manufacture of coal gas. This process requires the use of special plant, which may be described in outline as follows.

The coal is heated in horizontal tubular fireclay *retorts*, *a*, somewhat  shaped in section and six or more feet long. The open end of the retort is tightly attached to the iron furnace front *b*, which has for each retort a door *c*, through which coal can be shovelled in and coke removed, and also a vertical iron pipe, the *rising main d*, through which the gas is driven by the decomposition.

The retorts are generally arranged in groups of five for convenience of heating by a single furnace below each group, and are now generally tubular, with a door and rising main at each end.

In order to prevent the escape of gas during the charging of the retorts with coal, a curved pipe leads from the side of the rising main into a horizontal pipe, the *hydraulic main e*. This main contains condensed coal tar and water, below which the entering pipes dip, thus effectually sealing

themselves against small changes of pressure. The level of the liquid in this main is kept constant by allowing any excess to flow off into the *tar pit f*.

The gas given off contains vapour of the tar and ammonia, and is too hot to be purified. It is now passed through a series of pipes, the *condensers g*, at first of large diameter to condense the tar, and later of smaller diameter to cool the gas for complete purification and to remove more tar. All the condensed liquids are collected in the tar pit, and separate into two layers, the lower the gas tar, and the upper an aqueous solution containing ammonia and ammonium salts, the *gas liquor*.

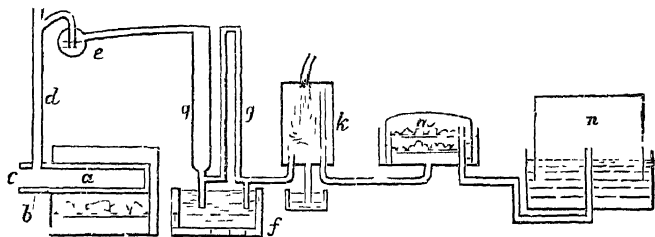


FIG 68.

From the condensers the gas rises through a larger vessel full of coke, the *scrubber k*, in which it meets a fine spray of water, which removes all traces of ammonia. This liquid, together with the gas liquor from the tar pit, is mixed with sulphuric acid to expel gaseous compounds of sulphur ( $\text{H}_2\text{S}$ , etc.) and to recover the ammonia in the form of ammonium sulphate.

After leaving the scrubber the gas passes through three to six feet of slaked lime contained in the *purifiers m*. These are square gas-tight iron tanks sealed with water, and containing the slaked lime spread on wooden grids in layers about six inches deep. The gas passes through this lime, which absorbs sulphuretted hydrogen and carbon dioxide, and other sulphur compounds, forming a mixture of calcium sulphide, carbonate, etc., the *spent lime* or *gas*

*lime.* To remove as much as possible of the sulphur compounds, the gas is generally passed through ferric hydroxide contained in another purifier, the ferric hydroxide is reduced to ferrous sulphide and sulphur is deposited. This mixture on being exposed to the air becomes oxidised, and may be used again until the sulphur is present in too great excess.

After leaving the purifiers the gas passes over into the *gas holders* *n*, where it is stored over water until it is required for use.

A ton of coal yields about 10,000 cubic feet of coal gas, which varies in composition, but contains approximately—

Hydrogen	.	..	..	50 per cent.
Marsh gas	...	...	...	35 "
Carbon monoxide	...	..	..	8 "
Ethylene, etc....	.	...	...	5 "
Nitrogen and oxygen.	.	.	...	3 "

Thus about 96 per cent. of the product has little or no illuminating power, this property being mostly due to the 5 per cent. of ethylene, etc.

**Coal tar** is a mixture of many organic substances which are separated by fractional distillation. Among the most important are benzene, naphthalene, anthracene, used in the manufacture of dyes, and phenol (carbolic acid).

**286 Coke.**—The residue in the retorts after the distillation of all the volatile products from coal is composed of two substances, *coke* and *gas-carbon*. The former is found in the centre of the retorts and consists principally of carbon, but contains all the non-volatile mineral matter present in the coal (*i. e.* the ash), and also small quantities of hydrogen, nitrogen and oxygen; the latter occurs as a deposit on the roof and sides of the retorts and is nearly pure carbon. Gas-carbon has been sufficiently fully treated in § 272. We shall, however, study coke at somewhat greater length.

The amount of ash in coke varies with the coal used, but the average composition is—

Carbon	..	..	...	...	91 5	per cent.
Hydrogen	.	.	...	..	0 4	„
Nitrogen and oxygen			...	...	2 1	„
Ash	...	...	...	...	6 0	„

**Exp 173**—Try to light a piece of coke in a flame: it does not burn so readily as coal, and requires a higher temperature to set it on fire

The temperature obtained by burning coke is very high, and, as there are no volatile products, there is generally neither luminous flame nor smoke from dry coke

Blue flames are often noticed playing above a brightly burning coke fire: these are flames of carbon monoxide, formed by the reaction between carbon dioxide and red-hot carbon.

Coke is not only obtained as a by-product in the manufacture of coal gas, but it is also specially manufactured by heating coal to redness in coke ovens. The coke so prepared is very dense and is used in iron smelting.

**287. Action of Heat on Wood.**—When wood is heated in the air it chars, gives off inflammable gases, and burns, leaving a black mass of charcoal, which slowly burns away.

**Exp 174**—Repeat Exp 172, using small pieces of wood (*e g* matchstalks) instead of coal dust. Note the formation of water, tar, inflammable gas and charcoal

Thus the distillation of wood and of coal in absence of air gives similar products, for we obtain wood gas, a water distillate, wood tar, and charcoal. *Wood gas* is used for illuminating purposes in Germany and Switzerland. The temperature of distillation must be very high, however, or the gas does not contain sufficient illuminating gases (heavy hydrocarbons) to be of any use for lighting purposes. The high temperature decomposes a large quantity of liquid oils which would simply distil over if a lower

temperature were used. This decomposition is helped by the use of cast-iron retorts instead of clay retorts.

The composition of wood gas as used for illuminating purposes varies between the following wide limits :—

Hydrogen	...	...	...	18 to 42 per cent.
Marsh gas	...	...	...	9 to 35 „
Carbon monoxide	...	...	...	22 to 62 „
Ethylene, etc	...	...	...	9 to 35 „

Practically no sulphur compounds are produced, but a considerable amount of carbon dioxide is given off, which is removed by slaked lime as in the case of coal gas.

The watery distillate contains only a small quantity of ammonia, but a number of organic substances are prepared from it, of which the chief are wood vinegar (acetic acid), wood spirit (methyl alcohol), and acetone

**Wood tar** contains many organic substances, of which creosote is the most important, the latter is used for the preservation of timber.

The residue left in the retort after the distillation is *wood charcoal*, which has already been described.

**288. Mineral Oils** —Reference has already been made to the naturally occurring mixture of hydrocarbons known as *petroleum* or *natural oil*. The constituents of this mixture have different boiling-points and may, therefore, be separated by distillation, the receiver being changed at intervals. The chief products are.—*Petroleum ether* (b. pt. 40°—70°), *gasoline* and *petrol* (b. pt. 70°—90°); these three fractions have a specific gravity 0.65—0.70; they are too inflammable for use as illuminants, but are employed as solvents for resins and oils in the manufacture of lacquers and varnishes and for the production of explosive mixtures in gas engines: *benzine* or *benzoline* (b. pt. 90°—120°; sp. gr. 0.70—0.74) is used for dissolving oils and greases and for small lamps; this fraction is also called *ligroin cleaning oil* (b. pt. 120°—170°) is used for the purpose which its name implies, and also instead

of turpentine in making varnishes: *kerosene* or *paraffin oil* (b. pt.  $150^{\circ}$ — $300^{\circ}$ ) is used for illuminating and heating purposes. The portion which distils over above  $300^{\circ}$  C. is partly liquid and partly solid at ordinary temperature. The liquid part is called *lubricating oil* and is used for lubrication. The solid is *paraffin wax*. It is separated from any adhering liquid by means of filter presses, and used in the manufacture of candles, night-lights, etc.

*Gasoline* is the residue which remains when some of the American petroleum is distilled *in vacuo* at low temperatures.

The oils obtained by distillation are generally free from sulphur, but are dark in colour. They are refined by agitation with sulphuric acid, followed by treatment with dilute caustic soda solution, by which means they are rendered nearly colourless and fit for use in lamps.

*Shale oil* is obtained by distilling *oil shale*, a bituminous shale found in large quantities in the coal measures in Mid-Lothian. The shale is broken up into small fragments and heated in vertical retorts, and the products of the distillation are passed through a condensing apparatus consisting of a long series of pipes, the arrangement being similar to that used in the manufacture of coal gas; the distillation is assisted by passing steam in at the base of the retorts. The liquid products collect in two layers, the lower consisting of an aqueous solution of ammonia and other substances, and the upper of oil and tar. The latter is a greenish brown mixture closely resembling petroleum, and on fractional distillation it yields a number of products which are very similar to those obtained from petroleum.

**289 Natural Gas**—In certain localities, particularly Pennsylvania in the United States, a natural gas which consists largely of hydrocarbons has accumulated in cavities in the earth's crust, and when borings are made which reach to these cavities, the gas, which is under great pressure, rapidly rises to the surface. This gas is largely used for illuminating purposes.



Oil gas is made by introducing that portion of shale oil which has a specific gravity of about 0.85 into retorts heated to bright redness, when the complex hydrocarbons of which the oil is composed are broken up, yielding a number of simpler gaseous hydrocarbons. Oil gas is much used for illuminating trains and for enriching coal gas.

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### QUESTIONS—CHAPTER XXI.

1. Show in tabular form the percentage of carbon and hydrogen in (a) wood, (b) peat, (c) lignite, (d) bituminous coal, (e) anthracite.
2. Taking the atmospheric pressure as 15 lbs. on the square inch, calculate the weight of carbon in a column of the air whose base is a square mile, the carbon dioxide present being 0.06 per cent. by weight.
3. Compare the densities of diamond, graphite and amorphous carbon. What do you regard as a full and sufficient proof that each of these bodies consists of the same element?
4. Describe how Moissan has succeeded in preparing artificial diamonds.
5. How would you prove that sugar contains carbon?
6. How is wood charcoal manufactured? Describe experiments illustrating its chief properties.
7. What is animal charcoal, how is it prepared, and for what purpose is it used?
8. How would you show by experiment that a hydrocarbon contains carbon and hydrogen, and that it consists entirely of these elements?
9. Where is marsh gas found to occur naturally, and how is it usually prepared in the laboratory?

- 10 How can it be proved that the formula for marsh gas is  $\text{CH}_4$ ?
11. Describe in detail the preparation of ethylene from alcohol
12. Explain the terms—*substitution compound, addition compound, unsaturated compound, saturated compound*
13. How may marsh gas be distinguished from ethylene?
14. Describe with equations the chemical changes which take place when ethylene is burnt in air and in chlorine.
15. Under what circumstances is acetylene formed during combustion of hydrocarbons? Can you suggest any means of determining the amount of acetylene in a mixture of hydrogen and acetylene?
- 16 How may acetylene be obtained in the pure condition?
- 17 What are the chief properties of acetylene, and for what purposes is it employed?
- 18 Describe how you would investigate experimentally the action of heat on coal in the absence of air.
- 19 Write a short account of the chief products of the destructive distillation of coal.
20. What are the chief products obtained from crude petroleum, and for what purposes are they employed?
- 21 State what you know about *natural gas* and *oil gas*
22. 0.1931 grammes of diamond gave on complete combustion 0.704 grammes of carbon dioxide. Calculate the percentage of ash in the diamond ( $\text{C} = 12$ ,  $\text{O} = 16$ ).
23. What volume of ammonia will be absorbed by 10 grammes of charcoal if the density of the charcoal is 1.5 and if it absorbs 172 times its volume of the gas?
24. 20 c.cs. of marsh gas are exploded with 50 c.cs. of oxygen. What will be the volume of the resulting gas? Also what diminution in volume will take place on treating the resulting gas with excess of caustic potash?

All volumes are supposed to be measured under standard conditions of temperature and pressure.

25. 30 c.cs. of ethylene are exploded with 150 c.cs of oxygen and the resulting gas treated with excess of caustic soda. What volume of gas will remain and of what will it consist?

All volumes are supposed to be measured at atmospheric temperature and pressure.

26. 10 c.cs. of acetylene measured at  $120^{\circ}\text{C}$  and 750 m.m. pressure are exploded with 80 c cs. of oxygen measured at the same temperature and pressure. What will be the volume of the resulting gas if the temperature and pressure suffer no change, and of what will it consist?

## CHAPTER XXII.

### COMBUSTION.

**290 Incandescence** —When the temperature of a body is raised to such a degree that it gives out light, it is said to be incandescent, or in a state of *incandescence*.

**Exp. 175** —Take pieces of platinum wire, iron wire, magnesium ribbon, black lead, charcoal, and some iron filings. Heat the first five and drop the filings through a flame, holding the burner aslant. In each case light is given out. While the platinum and iron wires and black lead return to the same state on cooling, the magnesium, charcoal and iron filings are changed by oxidation.

**Exp. 176** —Heat carefully about two grammes of ammonium bichromate in a porcelain basin, removing the flame as soon as a change takes place. Note that the change from red crystals to green powder is attended by incandescence.

Incandescence may thus be produced either by external heating or by the heat arising from chemical change.

Liquids and gases may also become so hot as to be incandescent, as in the flash seen during the explosion of a mixture of hydrogen and oxygen. The most common example of the incandescence of gases is afforded by flames.

**291. Flame.**—Whenever a gas or vapour is brought into an atmosphere with which it can react chemically, and the heat generated is sufficient to bring about incandescence of the particles, flame is produced. The heat is generated and the incandescence effected in the region where the reaction is carried on, that is, at the surface where contact occurs between the two gases, as is seen when a jar of hydrogen

burns mouth downwards. When we speak of hydrogen and coal gas as being combustible gases, and of air as being a supporter of combustion, we imply that hydrogen and coal gas, when once ignited, burn in air. In ordinary flames this is the case, we have seen, however, in Exp 168, that a jet of air can be made to burn in an atmosphere of coal gas

In either case the flame marks the surface of contact between the air and the coal gas, and is the region where the chemical changes take place which transform the hydrogen and carbon of the coal gas into water and carbon dioxide as ultimate products.

Where the gases are intimately mixed and then ignited the burning takes place with great rapidity, and an explosion of a more or less violent nature ensues, but where a regular supply of the combustible product impinges upon the atmosphere in which it burns, a more or less steady flame is the result, the particular form of which is determined by the nature of the jet and the shaping influence of air-currents.

**292 Point of Ignition.**—In any case, before flame can be produced at all, the temperature of the combustible body must first reach a certain limit known as the *point of ignition*. This temperature varies with different bodies the vapour of carbon bisulphide may be ignited by a glass rod heated only to  $150^{\circ}\text{C}$ ., whilst for hydrogen or coal gas a dull red heat ( $600^{\circ}\text{C}$ ) is insufficient.

**Exp 177** —Place in small basins or little tin saucers two or three drops of benzoline, a few drops of paraffin, and a small piece of paraffin wax, and apply a light to each. The benzoline burns at once, the paraffin oil must be slightly warmed, while the paraffin wax must be heated over a burner before it will light. In these cases the temperature of ignition is called the *flash point*

Conversely, a flame is extinguished if its temperature is by any means reduced below the point of ignition of the vapours consumed in it.

**Exp. 178** —Hold a piece of wire gauze (about thirty meshes to the inch) horizontally over a Bunsen burner and about an inch above the

orifice (Fig 69). Turn on the gas and light it on the upper side of the gauze. The flame will not be communicated to the stream of gas on the under side of the gauze.

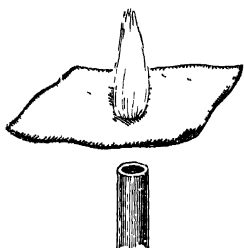


FIG 69

This is explained by the fact that the metal of the wire gauze is a good conductor of heat. The heat received from the flame is rapidly conducted away by the gauze and dissipated, chiefly by radiation. This continuous loss of heat prevents the temperature of the gauze from reaching the ignition point of the gas, and, as the gas below the gauze can only become heated by contact with the gauze, it does not become ignited.

**Exp 179** —Make a piece of the wire gauze into a cylindrical roll, and place a candle within it. Now direct the flame of a Bunsen burner against the outer surface of the gauze; the wax may be melted, but the candle cannot be lighted unless the gauze is heated to redness. The reason for this will be gathered from the explanation given in the previous experiment.

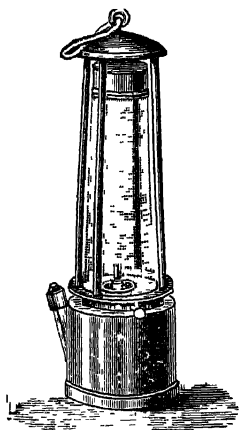


FIG. 70.

The *Davy Lamp* (Fig. 70) is a similar arrangement, in which an oil lamp is shut in by a layer of gauze; and, even if such a lamp be entirely surrounded with inflammable gas, this will not become ignited, although the inflammable gas which passes through the gauze may burn inside it and fill the space above the oil lamp with flame. If, however, the gauze becomes strongly heated, or if the flame should be mechanically driven through the meshes, communication

with the inflammable atmosphere outside may be established, and ignition will then take place.

**293. The Candle Flame.**—The inflammable matter in a candle is the wax or tallow, consisting of compounds containing carbon and hydrogen. The wax is melted and passes up into the wick, which serves as a still supplying the vapours of carbon compounds to the space immediately surrounding it. That such a space exists containing combustible vapours may easily be shown by the following experiment:—

**Exp. 180**—Depress a sheet of stout paper quickly into a candle flame to the level of the top of the wick, and hold it steadily there for about a second. On withdrawing it, a ring of sooty deposit will be seen, and within it a clear space. Secondly, take a glass siphon-tube, as shown in Fig. 71, and bring the shorter limb into the centre of the flame; presently yellowish-brown vapours will be seen to pass down the tube and issue at the other end. These vapours will be found to be inflammable, and may be burnt at the end of the tube.

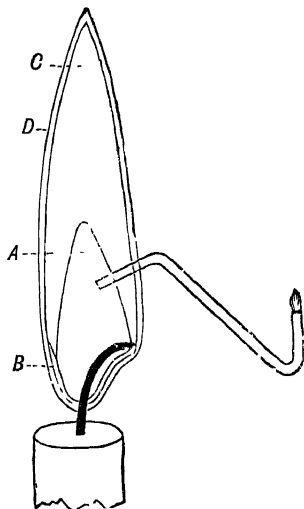


FIG. 71.

We can distinguish in the candle flame—

(1) A central zone surrounding the wick, and containing vapours of carbon compounds—the zone of no combustion (A in Fig. 71);

(2) A blue non-luminous zone, B, at the base;

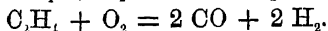
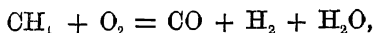
(3) A luminous zone, C, surrounding the dark central zone; and

(4) A faintly luminous mantle D. Under ordinary circumstances this zone is not easily seen, but if a little finely-powdered common salt is sprinkled over the flame, it will flash out as a golden-yellow fringe, the colour of which is due to the salt.

The mantle can also be seen as a golden band above the

wick by looking just above the glowing tip of the wick projecting through the side of the flame

The changes which take place in the different zones are somewhat as follows.—(A) Vapourisation of the carbon compounds. As these pass up this zone decomposition takes place, with gradual formation of acetylene and from it of dense hydrocarbons, and finally of free carbon particles. (B) The hydrocarbons present undergo partial combustion, with formation of carbon monoxide, hydrogen, and water—



(C) The changes which take place in this zone are very complex. The formation of dense hydrocarbons and separation of carbon particles is continued. Also incomplete combustion takes place with formation of carbon monoxide carbon dioxide, hydrogen, and steam. The luminosity of this zone is due to the presence of the solid carbon particles and dense hydrocarbons, which become incandescent owing to the heat evolved by the chemical reactions which are taking place. (D) Here the products of zones (B) and (C) are mixed with excess of air and burnt completely to carbon dioxide and water

**294. The Gas Flame**—A coal-gas flame has the same four zones as a candle flame unless the jet is very small. As its size is reduced the luminous zone gradually diminishes relatively to the non-luminous zones, and when the jet is very small it entirely disappears. The flame now consists of three zones only, and presents the appearance shown in Fig. 72.

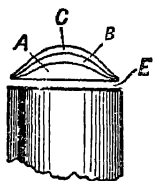


FIG. 72.

A is the zone of no combustion. B is the zone of incomplete combustion; it is blue, like zone B in Fig. 71, to which it corresponds. In the mantle C the combustion is complete. Between the flame and the burner there is a space E containing unburnt gas; it is part of the zone of no combustion.



**Exp. 181.**—Examine a gas-jet when turned on full, and note the zones as in the candle flame (§ 293). The mantle can be shown to be hot by means of a thin piece of wire held across the flame. Note the changes in the character of the flame as the gas is gradually lowered, and the gradual disappearance of the luminous zone.

**295. Luminosity of Flame**—There are three factors, some or all of which are concerned in the luminosity of flame—(1) the presence of solid particles; (2) the density of the flame gases, (3) the temperature. At one time it was believed that (1) and (3) were the sole causes; this was Davy's theory, and it was supported by the following facts:—

(a) Most flames in which no solid particles can be present are practically non-luminous: *e.g.* hydrogen burning in oxygen.

(b) Non-luminous flames become luminous when solid particles are introduced into them. *e.g.* finely-divided charcoal or lime blown into an oxyhydrogen blowpipe flame makes it luminous.

(c) A glass rod held in a candle flame becomes covered with soot only on the under side. If the interior of the flame consisted of vapours which deposited soot because they were cooled down by the rod, the deposit should be all round.

(d) Luminous flames, like that of a candle, when placed between a brighter light and a screen, cast a shadow, non-luminous flames cast no shadow.

That the luminosity of some flames is not due to the presence of incandescent solid particles is shown by the existence of luminous flames in which no solid matter can possibly be formed: *e.g.* the flame produced when phosphorus or phosphoretted hydrogen burns in oxygen, or arsenic burns in nitric oxide or oxygen. At the temperature of the flame in these cases all the possible products of combustion are gases. According to Frankland's theory, luminosity is due to the presence of heated gases, the luminosity increasing with the density of the gases. This is supported by the following facts:—

(a) A candle burns at high altitudes or in an artificially rarefied atmosphere with greatly-reduced luminosity.

(b) The flame of hydrogen burning in oxygen becomes luminous when the gases are under a pressure of two atmospheres

The effect of the temperature of a flame upon its luminosity may be studied by experiment.

**Exp 182** —Make a short coil of stout copper wire by giving it half-a-dozen turns round a piece of glass rod about 5 mm in diameter, leaving only a small space between one coil and the next. Bring the coil into the upper part of the luminous zone of a candle flame: the flame will become smoky, if it be quickly depressed to the level of the wick, the flame loses its luminosity, and, indeed, may be extinguished altogether

**Exp 183** —Fill a gas cylinder with oxygen and lower a lighted candle into it: the flame becomes much shorter and brighter.

In the first case, copper, which is a good conductor of heat, conveys away heat from the flame, and lowers its temperature to such an extent that the solid particles of carbon can no longer keep up their luminosity; they escape combustion and pass off as smoke. Indeed, the vapours may also be cooled below their ignition point, in which case the flame is extinguished altogether.

In the second case, the heat given out is not utilised in raising the temperature of the nitrogen of the air, but is all available for heating the particles of carbon.

Thus, raising the temperature of a flame increases its luminosity, and lowering its temperature decreases its luminosity

The effect of cooling is often noticed in very cold weather, when the gas, if carried by exposed pipes, does not possess its usual illuminating power: this is partly due to the condensation of volatile liquid and solid hydrocarbons contained in the gas, and also to the extra amount of heat required to raise both gas and air to the temperature of incandescence.

In ordinary flames used for various purposes all three causes operate and may be utilised.

**296. The Batwing and Fishtail Flames.**—In these flames the gas is made to issue from a narrow slit (fishtail) or from two jets which impinge on each other (batwing).

By these devices the flame is flattened. This enlarges the surface of gas exposed to the air, and thus increases the rate of combustion and the luminosity.

**297 The Bunsen Flame.**—This flame is produced by mixing air with the gas which is to be burned, in such quantity as to render the combustion nearly perfect and the flame non-luminous. The gas is supplied through a small jet placed inside a wide tube, so that the rush of gas sucks in air through holes at the bottom of the tube; the mixture of gas and air passes up the tube, and is ignited at its mouth.

There are two zones, both of which are non-luminous (Fig 73). In A (pale blue) incomplete combustion takes place, the hydrocarbons being in excess, and in B (very pale blue) the combustion is complete, air being in excess. The non-luminosity of a Bunsen flame is caused by (1) increased oxidation by which the separation of solid particles of carbon is prevented, or at any rate reduced; (2) dilution by the nitrogen of the air—this raises the temperature required for the decomposition of the hydrocarbons of coal gas, (3) cooling by the large volume of air introduced. The result of (2) and (3) is that the gases reach the outer zone where air is in excess and are completely burnt up, before they attain the temperature at which dense hydrocarbons are formed and carbon particles separate.

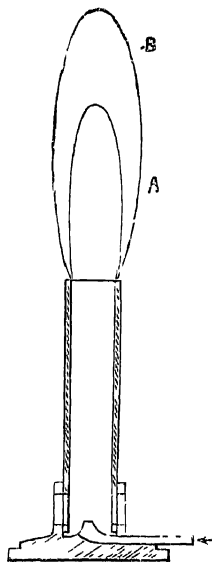


FIG 73.

**298. Oxidising and Reducing Flames.**—The foregoing paragraphs show that heated hydrocarbon vapours have the power of combining with oxygen in the gaseous condition to form carbon monoxide or dioxide, hydrogen, and water vapour. They have thus the power of abstracting oxygen from many solid oxides or bodies containing oxygen. This property may readily be shown either by means of the flame of a Bunsen burner or of the blowpipe.

**Exp 184** —Partially close the holes at the base of the Bunsen burner until there appears a well-defined luminous tip (A in Fig 74) within the flame owing to the reduction of the air supply. Now introduce within the luminous area a small amount of barium sulphate on a loop of thin platinum wire, and hold it there steadily for two or three minutes.

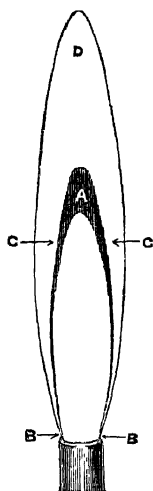


FIG. 74.

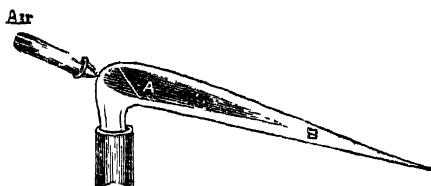


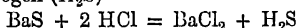
FIG. 75

In Fig. 74  
A is reducing area  
BCD is oxidising area  
B low temperature oxidising area  
C high " " "

In Fig. 75  
A is reducing area  
B is oxidising area

The substance will be found to have changed in character, for, whilst the barium sulphate originally taken is unacted upon by hydrochloric acid, the resulting body when moistened with dilute hydrochloric acid evolves an odour of sulphuretted hydrogen. The sulphate of barium ( $\text{BaSO}_4$ ) has been deprived of its oxygen, and has become barium sulphide ( $\text{BaS}$ ), this on treatment with dilute hydrochloric acid is

transformed into the soluble chloride of barium with the evolution of sulphuretted hydrogen ( $\text{H}_2\text{S}$ )—



Similarly, oxide of lead or copper may be reduced to metallic lead or copper when brought into the inner flame A of the blowpipe (Fig. 75). Wherever in a flame the hydrocarbons predominate and the supply of oxygen is limited such a *reducing* action prevails, and wherever in a flame the supply of oxygen is in excess of that required to consume the hydrocarbons, as in the outer zone of the candle or the Bunsen burner or the blowpipe flame, an *oxidising* action is experienced. This may be shown by bringing metallic tin or other metals into the outer margin of the Bunsen flame.

299. Definition of "Combustion."—The term *combustion* has hitherto been used in the popular sense to indicate the burning of a substance in air. Chemists, however, usually assign a broader meaning to the term, as follows:—*Combustion is chemical reaction between two substances accompanied by the production of heat and light.* There is no restriction as to the nature of the reacting substances. Some writers include under the term combustion such processes of oxidation as the rusting of iron in moist air, in which heat only, not light, is produced; but this is, perhaps, carrying the use of the term too far.

Usually the substance which is *outside* during the combustion is spoken of as a *supporter of combustion*, and that which is *inside* as the *combustible body*, but, as has been shown above in the case of coal gas and air, the supporter of combustion and the combustible body can change places. This holds also in other cases, so that the terms are only relative.

Since the external substance is usually air, a substance is commonly said to be combustible or not according to whether it will or will not burn in air. Thus, hydrogen, phosphorus, and carbon monoxide are combustible; chlorine and nitrous oxide are not combustible.

Again, a substance is said to be a *supporter of combustion* if it will allow the same substances to burn in it as burn

in air (*e.g.* coal gas, hydrogen, a taper) Chlorine and nitrous oxide are supporters of combustion, sulphuretted hydrogen, carbon monoxide, and hydrogen are not.

Strictly speaking, however, any two substances which can exist in the gaseous state and which can combine chemically with sufficient evolution of heat may occupy towards each other the positions of supporter of combustion and combustible body interchangeably. For example, a jet of hydrogen will burn in chlorine, and a jet of chlorine will burn in hydrogen. In the former case hydrogen is the combustible body and chlorine the supporter of combustion, in the latter the reverse. Again, phosphorus burns in oxygen, but it would be possible to burn oxygen in phosphorus vapour, in which case the latter would be the supporter of combustion.

**300 Heat of Combustion** — Whenever carbon, hydrogen, or bodies containing carbon and hydrogen burn, by combining with the oxygen of the air (the carbon to form carbon monoxide or dioxide, and the hydrogen to form water), the amount of heat accompanying the change is perfectly definite and constant.

If a gramme of pure carbon be burnt to carbon dioxide, the heat given out will be sufficient to raise the temperature of 8,080 c.c. of water  $1^{\circ}$  C.; this is expressed shortly by the statement that the *heat of combustion* of one gramme of carbon is 8,080 thermal units or calories. So, in like manner, the combustion of one gramme of hydrogen is found to give rise to the evolution of 34,200 thermal units. Hydrogen, therefore, on combustion gives out more than four times the amount of heat evolved by the same weight of carbon.

Bituminous coal consists chiefly of carbon, but, as it contains some hydrogen, it should give out more heat on combustion than the same weight of carbon, and it would do so but for the fact that it contains usually 15 to 20 per cent. of oxygen, sulphur, nitrogen, and mineral ash, which are practically unproductive of heat. In anthracite, however, these constituents amount to little more than 5 per

cent., and the heat of combustion of this kind of coal is greater than that of bituminous coal

Petroleum, consisting entirely of carbon and hydrogen, and containing much more hydrogen than coal, actually does give out more heat than the same weight of carbon.

Fuel being employed for heating purposes, the amount of heat generated in its combustion is of primary importance, and the following table shows at a glance the comparative value of different substances which are applicable as fuels :—

Hydrogen ..	34,200 thermal units	per gramme consumed.
Petroleum	12,000	”
Coal . .	7,500 to 8,500	”
Carbon .	8,080	”
Wood ...	about 3,000	”

### QUESTIONS.—CHAPTER XXII

1. Explain the term *incandescence*, and describe experiments which show how it may be produced
2. What conditions are necessary for the production and continuance of combustion? How would you show them experimentally?
3. Describe an experiment by which air may be made to burn in coal gas.
4. Explain what is meant by *point of ignition* and *flash point*.
5. Explain the principle of the *Davy lamp*, and describe an experiment which illustrates it.
6. Describe the structure of a candle flame, and explain the nature of the chemical changes which take place in the different zones.
7. Describe the appearance of a coal-gas flame which is burning very low.

- 8 Discuss the explanations which have been put forward to account for the luminosity of flame
- 9 Give a diagram of the Bunsen flame, and indicate on it
  - (a) the reducing area ;
  - (b) the oxidising area ,
  - (c) the high temperature oxidising area ;
  - (d) the low temperature oxidising area
- 10 What are the causes of the non-luminosity of a Bunsen flame ?
11. How may calcium sulphate be reduced to calcium sulphide
  - (a) in the blowpipe flame ;
  - (b) in the Bunsen flame ?
12. Explain carefully what you understand by *combustion*, and *supporter of combustion*.
13. What volume of water may be raised from 10° C. to 50° C. by the heat derived from the combustion of 10 grammes of hydrogen and 10 grammes of carbon respectively ?
14. Explain the term *heat of combustion*, and compare the heats of combustion of the common kinds of fuel.



## CHAPTER XXIII.

### OXIDES OF CARBON—CARBON BISULPHIDE.

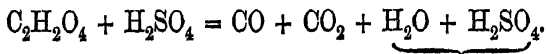
CARBON forms two compounds with oxygen, namely, carbon monoxide, CO, and carbon dioxide, CO<sub>2</sub>.

#### CARBON MONOXIDE, CO.

**301. Occurrence.**—This gas occurs in small quantity in chimney gases, especially where the air-supply during combustion is not in sufficiently large excess, it is also formed during the dry distillation of wood, coal, and such organic bodies. The gases from blast or other furnaces in which an excess of carbon is present, and in which a reducing operation is being performed, consist largely of carbon monoxide.

**302. Preparation from Oxalic Acid**—Carbon monoxide may be prepared by heating oxalic acid with concentrated sulphuric acid, an equal volume of carbon dioxide being given off at the same time.

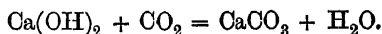
**Exp 185.**—Introduce about 20 grammes of crystallised oxalic acid into an 8-ounce flask provided with thistle funnel and delivery tube, and as much concentrated sulphuric acid as to cover it. Apply heat steadily until effervescence sets in, and then moderate it so as to secure a regular and not too rapid evolution of the gas. Collect over water, avoiding any escape of the gas, as it is very poisonous. The reaction which takes place is—



The sulphuric acid removes the elements of water from the oxalic acid without itself undergoing any chemical change

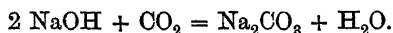
303. Experimental study of the products of the reaction—

**Exp 186.**—Pour lime-water into a jar of the gas, and shake up; the lime-water will become turbid owing to the formation of calcium carbonate \*—

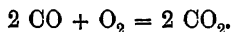


The presence of carbon dioxide is thus indicated.

**Exp. 187.**—Remove the cover from a jar of the gas, quickly pour in a few cubic centimetres of caustic soda, replace the cover and shake up well; the carbon dioxide will combine with the caustic soda, forming sodium carbonate—



Now bring the mouth of the jar under water, and remove the cover; the water will rise, and it will be seen that about half the volume of the gas is left. This is the carbon monoxide. Transfer some of this gas to a smaller vessel by decanting it over water, and shake up with lime-water, no turbidity will be produced, the carbon dioxide having been removed. Now apply a light to the gas; it will burn with a beautiful blue lambent flame. When the combustion is finished, again shake up the vessel, and marked turbidity will then be produced, showing that carbon dioxide has again appeared. The carbon monoxide has united with oxygen during the process of combustion, with the formation of carbon dioxide—



It may also be noticed that carbon monoxide does not itself support combustion, for if whilst it is burning the

\* After the experiment has been performed, it is well to burn the gas rather than to let it escape directly into the air.

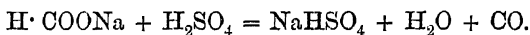
lighted taper be plunged into the vessel, the flame will be extinguished.

**Exp 188**—Remove the carbon dioxide from a second jar of the collected gas, and then decant into the jar sufficient air to fill the vessel.

We have now a mixture of equal volumes of carbon monoxide and air, and if after allowing the gases to stand for two or three minutes to mix properly, the mouth of the jar be held towards the flame of a Bunsen burner, it will be seen that carbon monoxide and air form an explosive mixture.

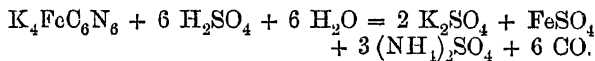
If it be desired to separate the carbon dioxide from the monoxide before collecting the gas this may be done by passing the gases evolved during its preparation through two wash-bottles containing caustic soda solution, as shown in Fig. 65.

**304. Other methods of preparation**—Carbon monoxide may, however, be prepared free from the dioxide by gently warming a mixture of sodium formate and sulphuric acid—



This is the method usually adopted in the laboratory.

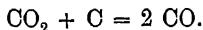
Another convenient method of preparation consists in heating roughly-powdered potassium ferrocyanide,  $\text{K}_4\text{FeC}_6\text{N}_6 + 3 \text{H}_2\text{O}$ , with concentrated\* sulphuric acid. The change which takes place is represented by the equation—



The water required for this reaction is derived partly from the water of crystallisation of the ferrocyanide and partly from the 1.5 per cent. of water present in the sulphuric acid.

\* *Dilute* sulphuric acid gives rise to the formation of hydrocyanic acid (HCN).

An interesting method whereby carbon monoxide may be obtained in large quantities, though in an impure condition, is to pass carbon dioxide over red-hot charcoal. The charcoal may conveniently be heated in an iron pipe by means of a combustion furnace, and the carbon dioxide evolved in a gentle stream by the action of hydrochloric acid on marble—



The carbon monoxide is either collected or burnt at a jet attached to the exit of the tube

This method of formation may be observed in a coke or red-hot cinder fire, on the surface of which the blue flames of the burning gas may be seen. The air passing in at the base of the fire at the lower part of the grate unites with carbon, forming carbon dioxide, and thus as it passes over the mass of red-hot carbon in the upper part of the grate is transformed into carbon monoxide. "Producer gas" or "generator gas," used in some manufacturing operations, consists largely of carbon monoxide, and is obtained by passing air over a high column of red-hot coke or anthracite.

When steam is passed over red-hot coke a mixture of carbon monoxide and hydrogen is formed, which is known as *water-gas*—



Water-gas is used on the large scale as a source of heat.

**305. Properties.**—Carbon monoxide is a colourless, tasteless gas; it is only very slightly soluble in water, 100 volumes of water at ordinary temperatures dissolving less than three volumes of the gas. It is also very difficult to condense, the liquid boiling under atmospheric pressure at  $-190^\circ \text{C}$ . Under ordinary circumstances, carbon monoxide burns in air, or may be exploded with oxygen in a eudiometer, forming carbon dioxide. But when the gases are *perfectly dried* by exposing them for a lengthened period to phosphorus pentoxide, sparks may be passed

through the mixture without combination taking place. This affords us with yet another example of the influence of moisture in assisting chemical reaction.

Owing to the readiness with which carbon monoxide combines with oxygen, it is a powerful reducing agent at high temperatures. It also combines directly with the vapour of sulphur, forming carbonyl sulphide (COS), and in sunlight with chlorine, forming carbonyl chloride ( $\text{COCl}_2$ ), also known as phosgene gas.

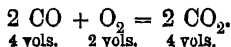
Finely-divided nickel and iron unite with carbon monoxide on heating, forming compounds called *carbonyls*, nickel carbonyl is represented by the formula  $\text{Ni}(\text{CO})_4$  and iron carbonyl by  $\text{Fe}(\text{CO})_5$ , both these compounds are liquids.

Carbon monoxide dissolves in a solution of cuprous chloride in strong hydrochloric acid or ammonia, with formation of a compound  $\text{Cu}_2\text{Cl}_2 \cdot \text{CO}$ . A solution of cuprous chloride is used as an absorbent for CO in gas analysis.

Carbon monoxide is a very poisonous gas, this property depending on its power of combining with the hæmoglobin of the blood to form a bright red compound, carbonylhæmoglobin.

**306. Composition** —The composition of carbon monoxide may be ascertained by exploding the gas in a eudiometer along with oxygen. It will be found that 100 volumes of carbon monoxide and 100 volumes of oxygen after explosion show a contraction to 150 volumes, and on absorbing the carbon dioxide formed by means of potash, 50 volumes of oxygen will remain. Thus 100 volumes of carbon monoxide have united with 50 volumes of oxygen to form 100 volumes of carbon dioxide.

This agrees with the formula CO for carbon monoxide assuming the formula for carbon dioxide to be  $\text{CO}_2$  (see § 311 for proof of this)—



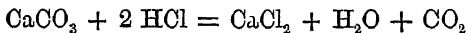
The density of carbon monoxide affords a confirmation of this formula. The gas is fourteen times as heavy as hydrogen, and therefore its molecular weight is  $2 \times 14$  or 28, that of hydrogen being 2.

Now C = 12, O = 16, and therefore CO = 12 + 16 or 28, so that, as already stated, CO is the correct formula for carbon monoxide.

### CARBON DIOXIDE (CARBONIC ACID GAS), $\text{CO}_2$ .

**307. Occurrence.**—This gas is of more frequent occurrence than carbon monoxide. Its presence in air and water has already been mentioned, and also the part it plays in the animal and vegetable kingdoms. It is given off in large quantities from lime-kilns, in which the limestone ( $\text{CaCO}_3$ ) is decomposed by heat into quicklime ( $\text{CaO}$ ) and carbon dioxide. Processes of fermentation and putrefaction give rise to the gas. Whenever an explosion of fire-damp occurs in coal mines carbon dioxide is formed in large quantities, and constitutes what the miners call the *after-damp* or *choke-damp*.

**308. Preparation.**—The usual method of preparing carbon dioxide, namely, by the action of dilute hydrochloric acid on limestone or marble, has already been described in Exp 57, § 41. The reaction which takes place is represented by the equation—



Although somewhat soluble in water, the gas may be collected over water, but as it is much heavier than air, it is usually collected by downward displacement. All carbonates, when treated with dilute hydrochloric acid, liberate carbon dioxide, many, such as limestone, liberate it when heated.

We have already seen that carbon dioxide is formed when carbon or compounds containing it are burnt in excess of air. If carbon compounds are heated to redness with oxide

of copper, the whole of the carbon is transformed into carbon dioxide, and it is in this way that the amount of carbon in such compounds is estimated.

**309. Properties of Carbon Dioxide.**—These have already been studied by experiment in § 41. Carbon dioxide is a colourless gas with a faintly acid taste and smell. It is about  $1\frac{1}{2}$  times as heavy as air, and its high density may be illustrated by the following experiment :—

**Exp. 189**—Fill a large beaker of three or four litres capacity by downward displacement with carbon dioxide ; now detach a soap-bubble charged with air into the beaker, and it will be found to float on the surface of the heavier carbon dioxide.

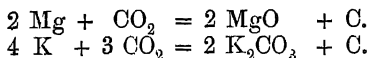
Carbon dioxide is soluble in water, which at  $15^{\circ}\text{C}$ . dissolves about its own volume of the gas, while at  $0^{\circ}\text{C}$  100 volumes of water dissolve 180 volumes of the gas. As with other gases, the amount dissolved increases directly as the pressure under which solution takes place, and soda-water being water charged with the gas under about four atmospheres pressure contains about four times its volume of the gas. The aqueous solution of carbon dioxide possesses feebly acid properties, for it is able to change the colour of litmus from blue to *claret* (not to the *bright red* produced by strong acids such as  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ ) ;  $\text{CO}_2$  can also, like other acids, decolourise phenol-phthalein which has been rendered pink by the addition of a small quantity of alkali.

**Exp. 190.**—Pass a stream of carbon dioxide through a few cubic centimetres of water to which some drops of litmus solution have been added, and note that the litmus assumes a claret tinge ; contrast this with the effect of adding litmus to water containing a little hydrochloric or sulphuric acid. Notice also that by boiling, the carbon dioxide is expelled, and the litmus assumes its original colour. A solution of carbon dioxide in water is therefore very unstable, and possessed of a feebly acid character.

**Exp. 191.**—Pass the expired air from the lungs, or carbon dioxide prepared from marble and washed free from hydrochloric acid by passing through water, through a slightly alkaline pink solution of phenol-phthalein, the pink liquid becomes colourless.

Carbon dioxide is in general a non-supporter of combus-

tion and of animal life. Certain metals, however, such as magnesium and potassium, will burn in it with liberation of carbon.



It is decomposed by the green colouring-matter of plants in presence of sunlight, carbon being assimilated and oxygen set free in the process.

Though the harmful effects of carbon dioxide are mainly due to suffocation (*i. e.* absence of oxygen), yet at the same time the gas does exercise a directly poisonous action on the system, for air containing more than one volume of it per thousand (*i. e.* about three times the normal quantity) has a distinctly depressing effect, and often gives rise to headache.

**310. Liquid and Solid Carbon Dioxide**—Under a pressure of 36 atmospheres at 0° C. the gas condenses to the liquid form, and in this form it is prepared on a tolerably large scale and stored in steel cylinders. If the nozzle of one of these cylinders be opened, the pressure being released, the liquid is rapidly transformed into gas. The amount of heat absorbed by the passage from the liquid to the gaseous condition is considerable, and the issuing gas becomes so far cooled that a part of it condenses again even to the solid form. Solid carbon dioxide is a white, snow-like substance which passes only comparatively slowly into the gaseous condition again. The depression of temperature caused by its passage from the solid to the gaseous condition is such that mercury can be readily cooled down to - 40° C. and obtained as a solid body.

**311. Composition of Carbon Dioxide**—This may be shown by a method similar to that employed in the case of sulphur dioxide. Thus when carbon is burnt in oxygen no change of volume occurs, and carbon dioxide is therefore said to contain its own volume of oxygen. It follows from Avogadro's hypothesis that the formula for the gas may be written  $\text{C}_x\text{O}_2$  where  $x$  has yet to be determined. Now the



molecular weight of carbon dioxide as deduced from its density is 44. This agrees with the value  $x = 1$  in the formula just given for  $C = 12$ ,  $O = 16$  and  $C_1O_2 = 12 + 2 \times 16$  or 44. The formula for carbon dioxide is therefore  $CO_2$ .

The composition by weight of the gas agrees with this formula, for, as already stated in § 265, 12 parts by weight of carbon unite with 32 parts of oxygen to produce 44 parts of carbon dioxide.

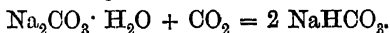
**312. The Carbonates.**—We have seen in a previous paragraph that a solution of carbon dioxide in water shows a feebly acid reaction. For this reason, and from a consideration of the salts known as the carbonates, carbon dioxide is to be regarded as the anhydride of carbonic acid, and the composition of the acid, although never isolated, may be taken as  $H_2CO_3$ .

Carbonic acid has two atoms of hydrogen replaceable by metals, and is therefore a *dibasic* acid. In the acid carbonates or *bicarbonates* only half the hydrogen is so replaced; thus  $KHCO_3$  is bicarbonate of potash, and  $NaHCO_3$  is bicarbonate of soda. In the normal carbonates the whole of the hydrogen is replaced, as with  $K_2CO_3$ , potassium carbonate, and  $Na_2CO_3$ , sodium carbonate.

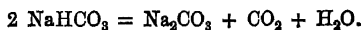
**Exp. 192**—Pass carbon dioxide to saturation into a solution of caustic soda, and then evaporate down to dryness on a water-bath. A residue will be obtained consisting of the monohydrated normal carbonate of soda,  $Na_2CO_3 \cdot H_2O$ .

Dissolve as much as possible of this in hot water and allow to cool, crystals of  $Na_2CO_3 \cdot 10 H_2O$  will be formed. This is the product known as "soda crystals," and used as washing soda.

On very gently warming a quantity of soda crystals, or preferably  $Na_2CO_3 \cdot H_2O$ , in an atmosphere of carbon dioxide, the salt takes up  $CO_2$  and is transformed into the bicarbonate,  $NaHCO_3$ —

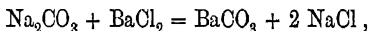


**Exp. 193**—Heat in a porcelain basin over the Bunsen flame a few grammes of dry bicarbonate of soda; carbon dioxide will be given off, and the normal carbonate reproduced—

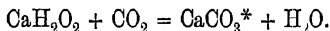


The carbonates and bicarbonates of the alkali metals are obtained by means of such reactions, they are soluble in water. The carbonates of other metals are insoluble in water, but the bicarbonates are soluble. Thus  $\text{CaCO}_3$  is insoluble, but  $\text{CaH}_2(\text{CO}_3)_2$  is soluble.

The insoluble carbonates may be obtained (1) by the addition of alkaline carbonates to a soluble salt of the metal—



(2) by passing carbon dioxide into a solution of the hydrate—



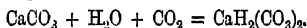
Weak bases such as alumina, oxide of silver, and oxide of mercury either form no carbonates or very unstable ones, and the normal carbonates of the alkali metals are the only ones which withstand a high temperature without decomposition. All other carbonates when heated give off carbon dioxide and form an oxide of the metal (except ammonium carbonate which decomposes into ammonia, carbon dioxide and water).

**313. Test for Carbonates.**—Add dilute hydrochloric acid to the solid carbonate, or an aqueous solution of a carbonate in a test-tube. An effervescence will be observed, and on decanting the gas downwards into a second tube containing lime-water, and shaking up, a turbidity will be produced in the lime-water owing to the formation of calcium carbonate.

**Distinction between Normal Carbonates and Bicarbonates.**—The test just given applies to both normal carbonates and bicarbonates. If, however, the carbonate is insoluble in water, it must be a normal salt. If it is soluble the following tests will decide to which class it belongs :—

(1) Add magnesium sulphate to the solution. Normal carbonates give an immediate white precipitate; bicarbon-

\* Excess of  $\text{CO}_2$  transforms this into the soluble bicarbonate—



ates only give a precipitate on boiling. (How do you explain this difference?)

(2) Boil the solution. Bicarbonates evolve carbon dioxide with effervescence, normal carbonates do not undergo decomposition.

### CARBON BISULPHIDE, $\text{CS}_2$ .

314. This compound occurs in traces in coal gas, and is formed in quantity when sulphur vapour is passed over red-hot charcoal. It is a colourless liquid, which refracts light strongly; it is very volatile, boiling at  $46^\circ \text{C}$  and giving off a very inflammable vapour. When pure it has a sweetish, ethereal smell, but usually the impurities which it contains render it very disagreeable. One of its most remarkable properties is its solvent action; india-rubber, fats, and some of the non-metallic elements such as phosphorus, sulphur and iodine, which are otherwise difficult to obtain in solution, are readily dissolved by bisulphide of carbon.

In consequence of its high refractive power for light, it is frequently employed as a means of producing a spectrum, the liquid being introduced into a hollow glass prism.

$\text{CS}_2$  is the analogue in composition of  $\text{CO}_2$ , and thiocarbonyl acid ( $\text{H}_2\text{CS}_3$ ), the analogue of carbonic acid ( $\text{H}_2\text{CO}_3$ ) is known, CS corresponding to CO has also been obtained. Thus a number of bodies are known containing sulphur in place of oxygen, the sulphur compound resembling the corresponding oxygen compound in chemical properties.

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### QUESTIONS—CHAPTER XXIII.

- 1 Mention some conditions under which carbon monoxide is produced during the combustion of fuel on the large scale
- 2 You desire to collect a specimen of CO as free as possible from air or  $\text{CO}_2$ , using oxalic acid as the source of the gas; how would you proceed?

3. What is the action of sulphuric acid on potassium formate? Give the equation.
4. What is the action of dilute and of concentrated sulphuric acid on potassium ferrocyanide?
5. How may CO be transformed into  $\text{CO}_2$  and  $\text{CO}_2$  into CO?
6. What is "generator gas," and how is it made? How would you show that it contains (a) CO, (b)  $\text{CO}_2$ , (c) H?
7. What is *water-gas*, and how is it manufactured?
8. It has been shown that chemical action undergoes modification when the reacting substances are perfectly dried, give instances of this.
9. How would you prove that carbon monoxide has the composition indicated by the formula CO?
10. What experiments would you perform in order to distinguish between
  - (a) CO and  $\text{CO}_2$ ;
  - (b)  $\text{CO}_2$  and a mixture of CO and  $\text{CO}_2$  containing large excess of  $\text{CO}_2$ ;
  - (c) CO and a mixture of CO and  $\text{CO}_2$  containing large excess of CO?
11. Write a short history of carbon dioxide.
12. Describe the reactions which take place when sodium bicarbonate ( $\text{NaHCO}_3$ ) and lead carbonate ( $\text{PbCO}_3$ ) are respectively subjected to the action of heat, and when they are brought into contact with dilute nitric acid.
13. Write down in separate columns (a) the physical, (b) the chemical properties of carbon dioxide.
14. Give two methods for the decomposition of carbon dioxide.
15. How may it be demonstrated that carbon dioxide has the formula  $\text{CO}_2$ ?
16. Are there any grounds for the assumption that  $\text{H}_2\text{CO}_3$  represents the composition of carbonic acid?
17. How are carbonates in general formed? Given metallic zinc, lime and caustic potash, how would you prepare specimens of zinc carbonate, calcium carbonate and potassium carbonate?

18. By what tests can *normal* carbonates be distinguished from *acid* carbonates?
19. What are the *characteristic* properties of bisulphide of carbon? What are the products formed, and their relative volumes, when this body is burnt in oxygen?
20. 15 c.cs. of carbon monoxide were exploded with 20 c cs. of oxygen. After treating the product with excess of caustic potash 12·5 c cs. of gas remain Deduce from this the formula for carbon monoxide assuming carbon dioxide to be represented by  $\text{CO}_2$ .

## CHAPTER XXIV.

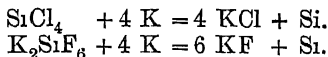
### SILICON AND BORON.

315 THESE two elements, together with carbon, closely resemble each other in many of their properties. Thus all of them exhibit allotropic modifications, one at least of which is crystalline and possesses a pronounced lustre; also, they are all very infusible. Each of them combines directly with oxygen to form an oxide possessing feebly acidic properties, but the union only takes place at high temperatures, especially in the case of the crystalline modifications

#### SILICON, Si.

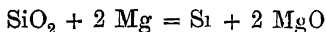
316. **Occurrence** — Silicon, occurring in combination with oxygen as silica ( $\text{SiO}_2$ ), is widely distributed, and forms the predominant constituent of many minerals and rocks. Quartz, agate and kieselguhr (a finely-divided siliceous material of organic origin) are essentially pure silica, whilst sandstone must be regarded as silica associated with varying quantities of oxide of iron, or alumina. Shale or clay consists of silica and alumina in more or less definite proportions, and a large body of mineral silicates of common occurrence, such as feldspar, serpentine, steatite, are very rich in silica. The element silicon is not found in the free state, and is not easy to isolate from its compounds, so that although it constitutes nearly one-fourth of the mass of the earth's crust it is yet a substance rarely met with even in the laboratory.

**317 Preparation**—Silicon is obtained by the action of sodium, potassium, or aluminium on silicon tetrachloride ( $\text{SiCl}_4$ ), or on potassium silicofluoride ( $\text{K}_2\text{SiF}_6$ ), in an atmosphere of hydrogen, or under such other conditions as to exclude oxidation—



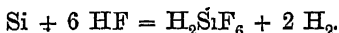
The residue is washed free from the potassium salts, which are readily soluble in water, and the silicon remains usually as a brown, amorphous powder.

Amorphous silicon is also obtained by heating sand and magnesium powder together in a glass tube when the magnesium combines with the oxygen of the silica and sets free silicon—

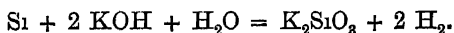


After cooling, the magnesium oxide is dissolved out from the mass by dilute hydrochloric acid, leaving a residue of silicon. Crystallised silicon is best prepared by heating sodium silicofluoride ( $\text{Na}_2\text{SiF}_6$ ) with sodium and zinc. The silicon set free by the action of sodium on the silicofluoride dissolves in the molten zinc, and, on cooling, separates out in needle-shaped crystals. To remove the zinc, the mass is treated with dilute hydrochloric acid; the sodium fluoride dissolves out at the same time.

**318. Properties.**—*Amorphous silicon* is a brown powder which can only be fused and volatilised at the temperature of the electric furnace. It burns on heating in air with formation of silica ( $\text{SiO}_2$ ). The only acid in which it dissolves is hydrofluoric acid; hydrogen is evolved and hydrofluosilicic acid ( $\text{H}_2\text{SiF}_6$ ) is formed—



Silicon is also dissolved by hot caustic potash solution with formation of potassium silicate and evolution of hydrogen—



Silicon combines directly with fluorine at the ordinary temperature with incandescence, forming silicon tetrafluoride ( $\text{SiF}_4$ ), it combines with chlorine on heating, yielding silicon tetrachloride ( $\text{SiCl}_4$ )

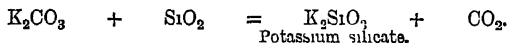
**Crystallised Silicon** is a very hard substance crystallising in dark-red rhombic octahedra, its specific gravity is considerably higher than that of amorphous silica. It does not burn in air even at very high temperature, but behaves towards fluorine and chlorine just as amorphous silicon does. It is insoluble in any single acid, but dissolves in a mixture of hydrofluoric and nitric acids.

### SILICON DIOXIDE (*Silica*), $\text{SiO}_2$ .

319 This is the only known oxide of silicon. It occurs in the *crystalline* form as quartz and tridymite, and in the *amorphous* form as opal, flint, and agate. It may also be prepared from certain mineral silicates, or silicates of the alkalis, by treating them with hydrochloric acid. It separates at first in the gelatinous form containing water, and if this gelatinous silica be heated the water is expelled, and anhydrous silica remains.

In the anhydrous condition, or in the mineral form, silica is unattacked by acids, with the exception of hydrofluoric acid; it can, however, be brought into solution again by fusion with alkaline carbonates.

**Exp. 194.**—Mix thoroughly together silica and about four times its weight of potassium carbonate, and heat in a platinum crucible over the flame of a Bunsen burner. Presently the mass swells up and evolves large quantities of carbon dioxide—



After heating for about half-an-hour, allow to cool, and extract with water, filtering off any insoluble matter (unattacked silica) which remains. The solution contains potassium silicate, together with potassium carbonate, which has been used in excess. Add strong hydrochloric acid to the solution until a marked acid reaction is obtained. If the solution be sufficiently concentrated, a flocculent precipitate of silica will be obtained. If, however, the solution be



dilute, no immediate precipitate is obtained, though one may separate on standing or by boiling. From such a solution a *soluble* form of silica may be prepared, as described in the next experiment. It is probable that the solution contains the compound  $\text{H}_2\text{SiO}_4$  called *orthosilicic acid*, but this acid has never been isolated. If the solution is left to evaporate *in vacuo* a translucent mass is left having the composition  $\text{H}_2\text{SiO}_3$  and termed *metasilicic acid*. It is tasteless and possesses only a very feeble acid reaction.

**Exp. 195.**—The solution contains potassium chloride, free hydrochloric acid and silica. Make a shallow dish by binding parchment paper over a hoop of tin or gutta-percha, float this on a considerable body of water (Fig. 76), and pour the liquid into it. The potassium chloride and hydrochloric acid will slowly pass through the membrane and diffuse into the water, while the silica will remain behind in solution in the dish.

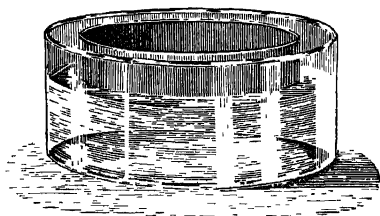


FIG. 76.

Sugar, salt and such bodies behave like potassium chloride, and readily pass through such a membrane, whilst white of egg, caramel and the like only do so extremely slowly. The former, from the fact that they are mostly crystallisable bodies, have been termed *crystalloids*, and the latter, from their gelatinous and amorphous nature, *colloids*. Silica is a colloid, and by means of this experiment it may be separated from such substances as common salt and potassium chloride, and obtained in solution. Under these circumstances we obtain silica in a form in which it is soluble in water.

There is, however, a third modification intermediate between these two, for when silica is freshly precipitated *in the cold*, it may be redissolved by the addition of dilute hydrochloric acid.

On standing, and more rapidly when boiled, this form becomes much less soluble, and ultimately passes into the insoluble variety.

To sum up we have—

(1) Mineral silica (crystalline or amorphous) and anhydrous silica insoluble in and unattacked by the ordinary acids, with the exception of hydrofluoric acid.

(2) Gelatinous silica, soluble in dilute acids.

(3) Dialysed silica, soluble in water.

320. **The Silicates.**—These salts are chiefly interesting from the fact that they are largely represented in the mineral kingdom; the following list indicates some of those of more common occurrence:—

(1) Silicates of magnesium.

Olivine,  $\text{Mg}_2\text{SiO}_4$ , or  $2 \text{MgO} \cdot \text{SiO}_2$ .

Talc,  $\text{Mg}_3\text{H}_2\text{Si}_4\text{O}_{12}$ , or  $3 \text{MgO} \cdot \text{H}_2\text{O} \cdot 4 \text{SiO}_2$ .

Serpentine,  $\text{Mg}_3\text{Si}_2\text{O}_7$ , or  $3 \text{MgO} \cdot 2 \text{SiO}_2$ .

(2) The Felspars

Orthoclase,  $\text{KAlSi}_3\text{O}_8$ , or  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6 \text{SiO}_2$   
(=  $2 \text{KAlSi}_3\text{O}_8$ ).

Albite,  $\text{NaAlSi}_3\text{O}_8$ , or  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6 \text{SiO}_2$   
(=  $2 \text{NaAlSi}_3\text{O}_8$ ).

Anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ , or  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2$ .

and the decomposition product of the felspars—

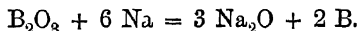
Kaolin,  $\text{H}_2\text{Al}_2\text{Si}_2\text{O}_8$ , or  $\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2$ .

A glance at this list is sufficient to show that the composition of the silicates is often very complex. With the exception of those of the alkalis they are all practically insoluble in water, and for the most part they can only be brought into solution either by treatment with hydrofluoric acid or by fusion with alkaline carbonates.

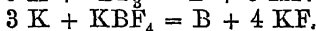
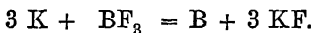
## BORON.

321. **Occurrence.**—Boron is not found free in nature; its chief naturally-occurring compounds are *boric acid*,  $\text{H}_3\text{BO}_3$ , *tincal* or native borax,  $\text{Na}_2\text{B}_4\text{O}_7 + 10 \text{H}_2\text{O}$ , *borocalcite*,  $\text{CaB}_4\text{O}_7 + 4 \text{H}_2\text{O}$ , and *boracite*,  $2 \text{Mg}_3\text{B}_8\text{O}_{15} + \text{MgCl}_2$ .

**Preparation**—Boron is prepared by reducing its oxide,  $B_2O_3$ , by means of sodium, potassium, or magnesium in an atmosphere of hydrogen—

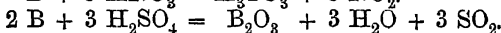
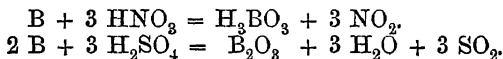


It is also obtained by the action of metallic potassium on boron trifluoride,  $BF_3$ , or on potassium fluoborate,  $KBF_4$  (heat being required in the latter case)—



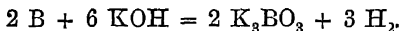
**Properties.**—Prepared by these methods boron is an amorphous brown powder, which is very difficult to fuse and not readily oxidised; on strongly heating in air, however, it burns, forming boron trioxide,  $B_2O_3$ , and boron nitride, BN.

Nitric acid and hot strong sulphuric acid both oxidise boron, the latter converting it into boron trioxide and the former into the corresponding acid,  $H_3BO_3$ —



The water produced in the latter reaction is taken up by the excess of sulphuric acid.

On fusion with the hydroxides or various salts of the alkali metals boron is also oxidised to boric oxide, which combines with the hydroxide to form a borate—

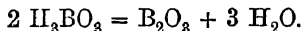


Like other non-metals, it is a bad conductor of electricity.

When mixed with aluminium, exposed to a white heat, and allowed to cool, the *crystalline* form of boron is obtained, the aluminium being removed by treatment with caustic soda. Prepared in this way it is, however, always associated with small quantities of carbon and aluminium.

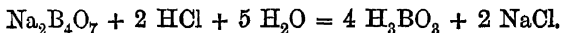
**322. Boron Trioxide,  $B_2O_3$ .**—This and the boric acid and borates derived from it are the most important of the boron compounds. The oxide is formed when boron is

burnt in air, but is usually prepared by heating boric acid to a high temperature—



Water is driven off and there remains a glassy-looking mass which when powdered combines slowly with water, forming boric acid ( $\text{H}_3\text{BO}_3$ ) again.

**323. Boric Acid, Orthoboric Acid, or Boracic Acid,  $\text{H}_3\text{BO}_3$** —The jets of steam, or *suffioni*, issuing from cracks in the ground in the volcanic regions of Tuscany contain a small quantity of boric acid. The dilute solution obtained by the condensation of the steam is concentrated in pans which are heated by some of the jets of steam. On cooling, impure boric acid crystallises out. Boric acid is also manufactured from tincal, which is decomposed by hot concentrated hydrochloric acid—

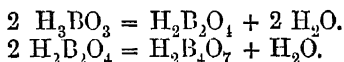


On cooling the acid separates out in thin laminæ.

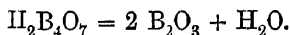
**Exp. 196**—Add concentrated hydrochloric acid to a hot strong solution of borax ( $\text{Na}_2\text{B}_4\text{O}_7 + 10 \text{H}_2\text{O}$ ). Allow to cool, filter off the crystals of boric acid which separate out and wash them with a little cold water. Note the soapy feel of the crystals.

**324. Properties.**—Boric acid is a crystalline solid slightly soluble in water and volatile in steam. It is a very weak acid which, like carbonic acid, gives with litmus a wine-red colour quite distinct from the bright red resulting from such acids as hydrochloric and sulphuric. Boric acid dissolves in alcohol and, on igniting, the alcohol burns with a green flame, due to the volatilisation of some of the acid. Its solution colours turmeric paper brown, and on drying and adding alkali the stain turns black.

On heating to  $100^\circ\text{C}$  boric acid loses water and is converted into *metaboric acid*,  $\text{H}_2\text{B}_2\text{O}_4$ , and on further heating to  $140^\circ\text{C}$ . more water is lost and pyroboric acid,  $\text{H}_2\text{B}_4\text{O}_7$ , is formed—



At a still higher temperature the remaining water is driven off, leaving boron trioxide or boric anhydride—



### QUESTIONS.—CHAPTER XXIV.

1. Mention any natural forms of silica either in the free state or in combination.
2. How are amorphous and crystalline silicon respectively prepared? With what elements does silicon combine directly?
3. Compare the properties of amorphous and crystalline silicon.
4. Under what circumstances is gelatinous silica obtained, and how may it be converted into the anhydrous form of silica?
5. How may a solution of silica be prepared and separated from any sodium chloride which may be associated with it?
6. Give a general description of the silicates, pointing out any characteristic properties which they possess.
7. Give two methods by which boron may be prepared. What is the action of the following substances on boron: (1) nitric acid, (2) sulphuric acid, (3) caustic potash? State the conditions under which the action takes place in each case and give equations.
8. Compare the allotropic forms of carbon, silicon and boron.
9. In what minerals does boron occur, and how may boric acid be obtained from these minerals?
10. What is the action of heat on boric acid?

## CHAPTER XXV.

### PHENOMENA OF ELECTROLYSIS.

325. SOME examples of Electrolysis have already been met with incidentally in the preceding chapters, but the more obvious phenomena of electrolysis should be studied more systematically. In the following explanations some knowledge of the elements of electricity is assumed.

**Electrolysis of Copper Sulphate.**—Fig. 77 represents dia-

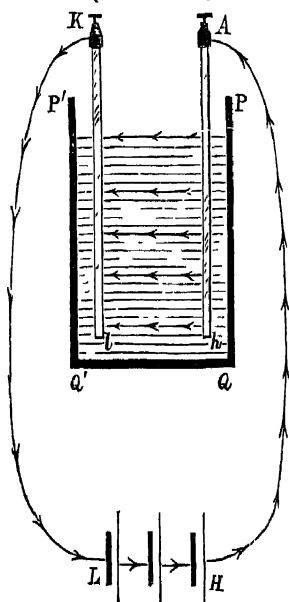


FIG. 77.

grammatically a simple experiment to illustrate electrolysis.  $PQQ'P'$  is a vessel containing a solution (in water) of copper sulphate. Immersed in the liquid are two platinum plates,  $Ah$  and  $Kl$ . These plates are connected by wires to the two poles of an electric battery  $LH$ —a Grove battery of two or three cells answers admirably. The “current” is assumed to flow in the direction represented by the arrows, viz. from  $H$  (the positive or copper pole of the battery) to  $A$ , down the plate  $Ah$ , through the liquid, up the plate  $Kl$ , from  $K$  to  $L$  (the negative or zinc pole of the battery), and back to  $H$  through the battery.

During the passage of the current chemical action takes place in the copper sulphate solution. Copper is deposited as a thin layer on the plate *Kl*, a gas is liberated at the plate *Al* (which can be collected and shown to be oxygen), and sulphuric acid gradually accumulates in the liquid.

Such an action—the decomposition of a liquid by an electric current—is called *electrolysis*, and the liquid is called the *electrolyte*. The vessel *PQQ'P'* is called the *electrolytic cell*. The two plates *Al*, *Kl* are called the electrodes. The plate *Al*, by which the current enters the cell, is called the *anode*, or the *positive electrode*. The

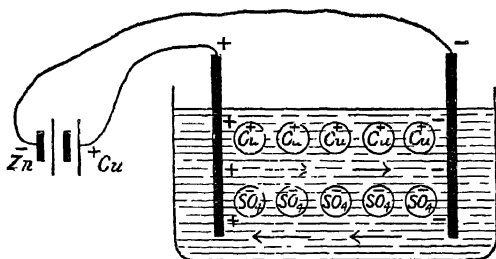


FIG 78.

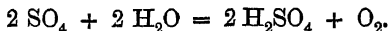
plate *Kl*, by which the current leaves the cell, is called the *kathode*, or the *negative electrode*. Note that the positive electrode is coupled with the positive pole of the battery, and the negative electrode with the negative pole.

The following explanation of the phenomenon just described is at present generally accepted.

It is supposed that when copper sulphate ( $\text{CuSO}_4$ ) is dissolved in water, some (in dilute solution the greater part) of the molecules are dissociated into two "ions." The one ion is the atom  $\text{Cu}$ , and the other is the group of atoms  $\text{SO}_4$ , which is called *sulphion*. The ion  $\text{Cu}$  is supposed to carry a *positive* charge of electricity and the ion  $\text{SO}_4$  a *negative* charge. When the electrodes are introduced into the liquids they attract the charged ions; the negative electrode attracts the positively charged ions, i.e. the copper ions,

and the positive electrode attracts the negatively charged ions, *i.e.* the sulphions. This is in accordance with the ordinary law of electric attraction. There is consequently a stream of Cu ions proceeding towards the negative electrode, and a stream of  $\text{SO}_4$  ions proceeding towards the positive electrode. This is represented diagrammatically in Fig. 78, in which  $\text{Cu}^+$  stands for a positively charged copper ion, and  $\text{SO}_4^-$  stands for a negatively charged sulphion.

When a Cu ion reaches the negative electrode it gives up its electric charge, and is deposited on the electrode as a thin film. At the same time an  $\text{SO}_4$  ion reaches the positive electrode and gives up its charge. An uncharged sulphion is, however, incapable of a separate existence, and immediately reacts with the water in contact with the positive electrode, with formation of sulphuric acid and liberation of oxygen.



The ion Cu, which is attracted to the cathode, is called the *kathion*; and the ion  $\text{SO}_4$ , which is attracted to the anode, is called the *anion*.

**326. Electrolysis in General.**—This process of electrolysis is very general in its application. All acids, alkalies and salts in the liquid state are electrolytes (whether naturally liquid or liquefied by heat or solution); that is to say, they will be decomposed by an electric current. In the case of salts, the kathion always consists of the atom or atoms of metal in the molecule, the remainder of the molecule forming the anion. In the case of acids, the kathion consists of the atom or atoms of hydrogen in the molecule.

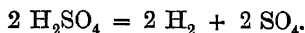
The properties of these ions are different from those of the substances as we ordinarily know them; *e.g.* ionic sodium does not decompose water. But when the ions reach the electrodes their charge is neutralised, and they resume their normal chemical properties. Hence it frequently happens that further chemical action takes place at one or both electrodes between the discharged ions and the liquid or the metal of which the electrodes are composed.



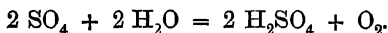
**327. Electrolysis of Water.**—Pure water does not conduct electricity, but when an acid, base or salt is dissolved in it, it becomes an electrolyte.

An experiment in which water acidulated with dilute sulphuric acid is decomposed by the electric current has already been described in § 32. The part played by the sulphuric acid is explained as follows—The acid on solution dissociates into three ions, two of hydrogen (H) and one of sulphion ( $\text{SO}_4$ ). The H ions carry positive charges of electricity and the  $\text{SO}_4$  ion a negative charge. On passing the current, the H ions are attracted to the negative electrode, where they give up their charge and acquire the properties which we ordinarily associate with hydrogen. One of these is that free atoms of hydrogen cannot exist separately; they therefore combine to form molecules, in which form the gas passes off and may be collected. The sulphions are attracted to the positive electrode, and after giving up their charges undergo a secondary reaction with water with liberation of oxygen, as already described in the previous paragraph.

Let us start with, say, two \* molecules of sulphuric acid, and trace the changes which they undergo. We may represent the primary change which takes place on passing the current by the equation—



The  $2 \text{H}_2$  is evolved at the kathode and the  $2 \text{SO}_4$  liberated at the anode reacts with water thus—



The  $\text{O}_2$  is evolved at the anode.

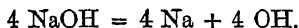
We therefore finish with the same amount of sulphuric acid with which we started, *i. e.* 2 molecules, and the net result of passing the current has been to break up two molecules of water into two molecules of hydrogen and one molecule of oxygen. The same result would have been

\* Two molecules are used instead of one to avoid writing an *atom* of oxygen in the second equation.

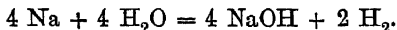
arrived at if we had taken any other number of sulphuric acid molecules, from which it follows that the amount of sulphuric acid in the cell remains unchanged, and the gases ultimately liberated are the constituents of pure water.

**328. Electrolysis of Hydrochloric Acid**—If strong hydrochloric acid be substituted for dilute sulphuric acid the ions are hydrogen and chlorine. On passing the current, hydrogen at once appears at the kathode, but no chlorine makes its appearance, for two reasons: firstly, because chlorine is soluble in the acid solution; and, secondly, because the chlorine, while still in the condition of free atoms (*nascent* chlorine), attacks the platinum anode, converting it into the soluble platinum chloride ( $\text{PtCl}_4$ ). If the anode be a plate of gas carbon, on which chlorine, even when nascent, has no action, and if the solution be saturated with chlorine beforehand, hydrogen and chlorine appear in equal volumes, as we saw in Exp. 123

**329. Electrolysis of Solutions of Alkalies.**—When caustic soda ( $\text{NaOH}$ ) dissolves in water it separates into the two ions, sodium and hydroxyl ( $\text{OH}$ ). On passing a current through the solution the former is liberated at the kathode and the latter at the anode. Neither of these, however, appears, because of secondary actions, the sodium immediately decomposing water with evolution of hydrogen and re-formation of caustic soda, and the hydroxyl breaking up into oxygen, which escapes, and water, which remains. Considering the changes which four\* molecules of  $\text{NaOH}$  undergo we have as the primary change on passing the current—

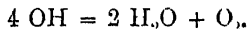


The following secondary changes then take place. At the kathode—



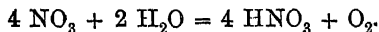
\* Four molecules are used for a similar reason to that referred to in the foot-note on p. 361.

At the anode—



The net result is that the amount of caustic soda remains unchanged and water is decomposed into hydrogen and oxygen. It will, therefore, be seen that the electrolysis of dilute sulphuric acid and of caustic soda solution both bring about the same result, namely, the decomposition of water.

**330. Electrolysis of Solutions of Salts.**—Here the immediate products of the decomposition (ions) are the metal and the acid radicle— $\text{SO}_4$ ,  $\text{Cl}$ ,  $\text{NO}_3$ , etc.—the former, like the metal of an alkali and the hydrogen of an acid, always going to the kathode, and the latter always going to the anode when the current is passed. But whether these ions actually appear or not after giving up their charges to the electrodes, depends upon the nature of the ions and the presence or absence of secondary actions between them and the liquid or the electrodes. Except in the case of those metals which decompose water at the ordinary temperature ( $\text{Na}$ ,  $\text{K}$ , and a few others), the metal is always deposited on the kathode; but, except in the case of some of the hydracids ( $\text{HCl}$ ,  $\text{HI}$ , etc.), the acid radicle rarely appears as such, even if no action takes place between it and the anode. In the case of sulphates, as we have seen, the acid radicle  $\text{SO}_4$  reacts with water forming sulphuric acid, with liberation of oxygen. In the case of nitrates the radicle  $\text{NO}_3$  behaves in a similar manner, yielding nitric acid and liberating oxygen—



If a solution of zinc sulphate ( $\text{ZnSO}_4$ ) be electrolysed between platinum electrodes, zinc is deposited on the kathode, and for every atom of zinc deposited an atom of oxygen is liberated at the anode and a molecule of sulphuric acid goes into solution. But if a plate of zinc replace the platinum anode, the  $\text{SO}_4$  group, instead of reacting with water, simply combines with the zinc to form  $\text{ZnSO}_4$ .

Then for every molecule of  $\text{ZnSO}_4$  decomposed, and for every atom of zinc deposited at the kathode, an atom of zinc is dissolved and a molecule of zinc sulphate re-formed at the anode; so that the kathode gains exactly as much zinc as the anode loses, and the average composition of the solution remains unaltered.

With copper sulphate ( $\text{CuSO}_4$ ) electrolysed between copper electrodes the action is less simple. Copper is deposited on the kathode, but at the anode some of the  $\text{SO}_4$  directly unites with the copper to re-form copper sulphate, and some reacts with water forming sulphuric acid, with liberation of oxygen. And of this oxygen some escapes, while some unites with the copper to form copper oxide ( $\text{CuO}$ ), which in part incrusts the plate, and in part dissolves in the acid to re-form copper sulphate—



**331. Electro-chemical Equivalents.**—If the same current be sent successively through several electrolytic cells containing solutions of salts of different metals, all those metals will be deposited in amounts proportional to their chemical equivalents

Take three electrolytic cells containing respectively (a) acidulated water, (b) a solution of silver nitrate, (c) a solution of copper sulphate. Connect them in series with a battery so that the whole current passes through each cell in succession. Find the weight of hydrogen liberated in (a), of silver deposited in (b), and of copper deposited in (c). Suppose these weights are respectively 0.01038 gramme, 1.112 grammes, and 0.3281 gramme.

We can now determine the weight of silver and of copper deposited for each gramme of hydrogen liberated. Thus—

$$1.112 \div 0.01038 = 107.1 \text{ for silver.}$$

$$0.3275 \div 0.01038 = 31.55 \text{ for copper.}$$

Such numbers may be termed the *Electro-chemical Equivalents*. A more complete list is given in the following table, together with the atomic weights:—

**Table of Electro-chemical Equivalents, together with Atomic Weights.**

Gold ...	Equivalent	65.2	...At. Wt.	195.7
Silver ..	„	107.1	... „	107.1
Copper ..	„	31.55	... „	63.1
Mercury	„	99.25 and 198.5	.. „	198.5
Tin ...	„	29.5 and 59.0	. „	118.1
Iron ...	„	18.5 and 27.75	. „	55.5
Zinc .	„	32.45	... „	64.9
Lead ...	„	102.7	... „	205.3

An examination of the table shows—

(1) That the electro-chemical equivalent is either equal to the atomic weight or some definite fraction of it ;

(2) That in some cases the same element gives more than one value. In these cases the values are found to correspond with the equivalent of the element in the particular compound electrolysed.

It was also found by Faraday, by whom these relationships were discovered, that the amount of an element deposited bears a definite proportion to the amount of the current of electricity. These facts are embodied in what are known as Faraday's Laws of Electrolysis :—

(1) The quantities of the elements deposited in the same circuit are chemically equivalent ,

(2) The quantities deposited are proportional to the current.

**332. Useful Applications. Electro-deposition.**—The principle of electrolysis has many useful applications in the arts. One of the oldest of these is the process of *electro-plating*. Here the object to be plated is thoroughly cleaned and slightly roughened, and made the kathode of an electrolytic cell, the anode being a plate of the metal to be deposited, and the electrolyte a solution of a salt of that metal, the current being supplied by a battery or dynamo. A thin and firmly adherent film of the metal

—gold, silver, nickel, or what not—is deposited on the article to be plated, and the strength of the solution is kept up by the action of the electrolyte on the anode. Compare with this the above description of the electrolysis of zinc sulphate, when a zinc anode is used.

The most important electro-plating industry is *electro-silvering*. In this case the salt is a double cyanide of silver and potassium, the “bath” being prepared by dissolving one part (by weight) of silver cyanide and two of potassium cyanide in 40 of distilled water. The current is maintained until the deposit amounts to about one ounce per square foot, which corresponds to a thickness of about  $\frac{1}{800}$  inch.

*Electro-gilding* is the art of coating objects with gold. The bath is a solution of the double cyanide of gold and potassium. The details are similar to those for electro-silvering, except that the current employed is weaker and the deposit thinner.

*Electro-nickeling* is the art of coating objects (usually of steel, such as the handle-bars of bicycles) with nickel. The bath is a slightly acid solution of the double sulphate of nickel and ammonium. A good coat consists of about  $\frac{3}{4}$  ounce per square foot, which represents about  $\frac{1}{1000}$  inch in thickness.

*Electro-coppering* is the easiest of all the plating processes. The bath is simply a strong and very slightly acid solution of copper sulphate. When *iron* is the metal to be coppered the simple copper sulphate bath is unsuitable, because the sulphate would be rapidly decomposed by the iron; in this case the bath consists of an alkaline solution of the double tartrate of copper and sodium obtained by adding excess of sodium hydroxide to a solution of copper sulphate and tartaric acid.

In *electrotyping*, the object is to produce not a thin adherent coat, but a thick one, which may be readily detached from the mould which serves as the cathode, and which reproduces, with the utmost fidelity, all the form and relief of the original article. Engraved wood blocks, for instance, are thus reproduced in copper. A mould is

first prepared in gutta-percha, plaster of Paris, or some other substance. The face of this mould is then black-leaded to form a conducting film, and the mould is hung in a solution of sulphate of copper, in which it becomes the kathode, the anode being a sheet of copper suspended in the solution. When the deposited copper forms a layer of sufficient thickness it is removed from the mould, backed with type metal, and mounted type-high on a wood block.

333. **Electrometallurgy.**—Many metals are now economically extracted from their compounds by electrolysis—sodium, for instance, the electrolyte being caustic soda melted by heat. Sodium and hydrogen separate at the kathode, the latter being allowed to escape, and oxygen at the anode. Aluminium is similarly obtained by the electrolysis of alumina dissolved in a bath of molten fluorides of aluminium, sodium and calcium. Crude copper is also economically refined by using it for an anode, and re-depositing it in a state of purity upon rods or sheets of copper which serve as kathodes. In these cases the current is derived from a dynamo driven by steam- or water-power.

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### QUESTIONS.—CHAPTER XXV

1. Describe what you would observe when a current of electricity is passed through aqueous solutions of the following substances, using platinum electrodes :—  
(1) copper sulphate ; (2) sulphuric acid ; (3) caustic potash.
2. Explain the meaning of the terms—*electrolysis*, *ion*, *anode*, *kathode*.
3. What do you understand by an *electrolyte* ? Describe and explain as far as you can what takes place when an electric current is passed through (i) a solution of caustic soda, (ii) fused caustic soda.

4. Give an account of three different cases of preparing chemical elements by electrolysis, with the precautions to be taken for collecting the products.
5. Describe and explain what takes place when a current of electricity is passed through a solution of zinc sulphate between platinum electrodes.
6. The same electric current is passed through solutions of copper sulphate and stannic chloride. What will be the relationship between the weights of metals deposited, and what laws do they illustrate?
7. Give Faraday's Laws of Electrolysis, and explain how you would prove them.
8. Describe a method of determining the *electro-chemical equivalent* of copper. Explain the meaning of the term.
9. Write a short account of the applications of the principle of electrolysis which have been made in the arts.



# CHAPTER XXVI.

## MODES OF FORMATION OF SALTS.

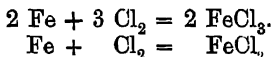
334. **Definitions of the Term "Salt."**—In Chapter XII we defined a salt as a substance produced by replacing the hydrogen of an acid by a metal. We may now, in the light of the electrolytic theory discussed in the previous chapter, give another definition, viz. a salt is a substance which when dissolved in water breaks up more or less completely into two ions, one of which is a metal or group of elements equivalent to a metal (*e. g.*  $\text{NH}_4$ ), and the other a non-metal or a non-metallic radicle (*e. g.*  $\text{SO}_4$ ). This definition includes both acids and bases,\* as well as the substances which are usually termed salts, for in a solution of an acid the hydrogen acts as a metallic ion, and in a solution of a base the hydroxyl radicle constitutes the non-metallic ion. An example will illustrate the relation between the three classes of bodies—

	Metallic ion	Non-metallic ion
Nitric acid.	$\text{H}^+$	$\text{NO}_3^-$
Caustic potash.	$\text{K}^+$	$\text{OH}^-$
Potassium nitrate.	$\text{K}^+$	$\text{NO}_3^-$

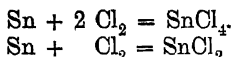
\* *Oxides* are of course not included. Some chemists, however, restrict the term *base* to metallic *hydroxides*.

**335 Modes of Formation of Salts.**—Many examples of the various ways in which salts are formed have been given in the foregoing pages. We shall now collect these methods together and classify them.

**Method 1. Direct Union of a Metal and a Non-metal.**—This method is largely employed for the production of the anhydrous salts of the halogen acids, since most metals unite directly with the halogens. When the metal forms two salts, one containing a higher percentage of halogen than the other, it depends upon the relative masses of the metal and the halogen which react, whether the higher or the lower salt is formed. Iron, for instance, yields ferric chloride ( $\text{FeCl}_3$ ) with excess of chlorine; but if the iron is in excess, ferrous chloride ( $\text{FeCl}_2$ ) is formed—



Similarly, tin yields stannic chloride ( $\text{SnCl}_4$ ) or stannous chloride ( $\text{SnCl}_2$ ), according as chlorine or the metal is in excess—



The combination of mercury and iodine affords another example,  $\text{HgI}_2$  or  $\text{Hg}_2\text{I}_2$  being formed according as iodine or mercury is in excess

Many sulphides can also be readily obtained by the direct union of metals with sulphur (see §§ 45, 219)

**Method 2. Interaction of Metals and Acids.**—When acids act on metals, a salt of the metal is almost invariably obtained as one of the products. In some cases, *e.g.* when dilute hydrochloric, dilute sulphuric, or acetic acid acts on magnesium, zinc or iron, hydrogen is the only other product, and these reactions are used in the preparation of hydrogen, as we have seen. In other cases the reactions are more complex, and these have been fully discussed in §§ 190, 236.

The action of a haloid acid on a metal always results in the formation of its *lower* salt when it forms more than

one. Thus, with hydrochloric acid, iron forms ferrous chloride,  $\text{FeCl}_2$ , and with tin it forms stannous chloride,  $\text{SnCl}_2$ . We should expect this because the nascent hydrogen which is liberated in the reaction is a strong reducing agent, and would immediately reduce the higher salt if any were formed.

When the acid is a strong oxidising agent, *e. g.* nitric acid, the nascent hydrogen which may be supposed to be liberated at first is immediately oxidised to water, and it depends upon the relative masses of the metal and the acid whether the lower or the higher salt is formed. This may be illustrated by the following experiments.

**Exp 197.**—Warm a small quantity of mercury with excess of nitric acid till the metal has dissolved. Now add hydrochloric acid to the solution; no precipitate will be formed, proving the absence of any mercurous nitrate (which with hydrochloric acid would form a white precipitate of mercurous chloride). The mercury has been entirely converted into mercuric nitrate.

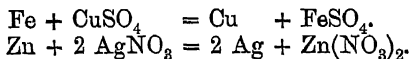
**Exp 198.**—Next allow some mercury to remain in contact with about half its volume of dilute nitric acid for some time. Pour off the supernatant liquid from the mercury and add hydrochloric acid, a white precipitate is at once formed, showing that when the mercury is in excess of the acid, it is converted into mercurous nitrate.

Salts of the haloid acids may be obtained by acting on a metal with either the gaseous acid or its aqueous solution; if the anhydrous salt is required, only the former method can be employed in many cases, because, on evaporating the aqueous solution of the salt to dryness to drive off water, the salt undergoes decomposition. Aluminium chloride, for instance, is decomposed by water on evaporation to dryness, with formation of aluminium hydroxide,  $\text{Al}_2(\text{OH})_6$ , and hydrochloric acid—

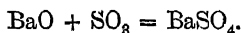


**Exp. 199**—Dissolve some aluminium in hydrochloric acid and evaporate the solution to dryness in a porcelain dish on a sand-bath. Try to dissolve the white residue in water; it is insoluble (whereas aluminium chloride is soluble) and consists of aluminium hydroxide formed according to the equation given above.

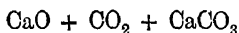
**Method 3. Interaction of a Metal with a Salt of Another Metal**—In general one metal will displace another from its salts when the oxide of the former is more strongly basic than that of the latter, *i.e.* the oxide reacts more readily with acids. Thus iron displaces copper from a solution of copper sulphate, and zinc displaces silver from a solution of silver nitrate, as we saw in Experiments 1 and 2—



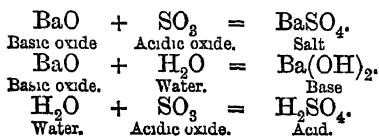
**Method 4. Direct Union of a Basic Oxide and an Acidic Oxide**—Many basic oxides combine directly with acidic oxides to form salts. For example, when barium oxide, BaO, and sulphur trioxide, SO<sub>3</sub>, are mixed together they combine to form barium sulphate with such energy that the mass becomes red-hot—



Again, quicklime and carbon dioxide readily unite to form calcium carbonate—

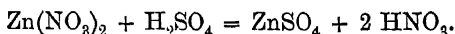


Adopting the broad definition of a salt which follows, as shown above, from the electrolytic dissociation theory, we may include the formation of acids from acidic oxides and water, and bases from basic oxides and water under this heading; in the formation of acids in this way water plays the part of a basic oxide, and in the formation of bases that of an acidic oxide. Thus, just as barium oxide combines with sulphur trioxide to form barium sulphate, so it combines with water to form the base barium hydroxide, Ba(OH)<sub>2</sub>; and just as sulphur trioxide combines with barium oxide to form barium sulphate, so it combines with water to form hydrogen sulphate or sulphuric acid.

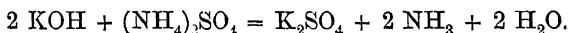


**Method 5. Interaction of Bases and Acids.**—This is the most general method. It is fully discussed in § 86.

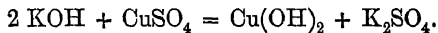
**Method 6 Interaction of an Acid with a Salt of a more Volatile Acid.**—An example of this method is the conversion of a nitrate into a sulphate by heating with strong sulphuric acid. The volatile nitric acid is driven off, leaving the salt of the much less volatile sulphuric acid behind. Zinc nitrate,  $\text{Zn}(\text{NO}_3)_2$ , may in this manner be converted into zinc sulphate,  $\text{ZnSO}_4$ —



**Method 7. Interaction of a Base with a Salt of a more Volatile Base**—When caustic potash or soda is heated with an ammonium salt, the volatile base, ammonia, is driven off and the corresponding potassium salt remains—

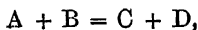


**Method 8. Interaction of a Base with a Salt of an Insoluble Base.**—The majority of the hydroxides of the metals are insoluble in water. If, then, a solution of a soluble base such as caustic potash or soda is added to a salt of a metal which forms an insoluble hydroxide, double decomposition takes place with precipitation of the insoluble hydroxide and formation of a salt of potassium or sodium; for it is observed that, *when an insoluble substance can be formed by double decomposition, that substance is usually formed.* For example, on adding caustic potash to a solution of copper sulphate,  $\text{CuSO}_4$ , cupric hydroxide,  $\text{Cu}(\text{OH})_2$ , is precipitated, and potassium sulphate,  $\text{K}_2\text{SO}_4$ , goes into solution—

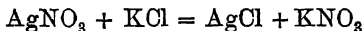


The  $\text{K}_2\text{SO}_4$  can be separated from the  $\text{Cu}(\text{OH})_2$  by filtration.

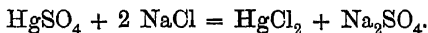
**Method 9. Interaction of Two Salts**—Representing the double decomposition between two salts by the equation—



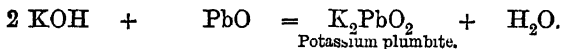
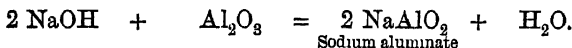
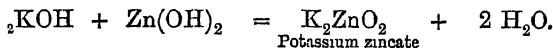
this method of preparation can be used for a salt, C, when that salt is less soluble or more volatile than A, B, or D. For example, silver chloride,  $\text{AgCl}$ , is insoluble in water, whereas silver nitrate,  $\text{AgNO}_3$ , potassium chloride,  $\text{KCl}$ , and potassium nitrate,  $\text{KNO}_3$ , are all soluble. We can therefore prepare silver chloride by mixing solutions of silver nitrate and potassium chloride, silver chloride is precipitated and may be separated from the soluble salts by filtration—



Again, mercuric chloride,  $\text{HgCl}_2$ , is volatile, whilst sodium chloride, sodium sulphate,  $\text{Na}_2\text{SO}_4$ , and mercuric sulphate,  $\text{HgSO}_4$ , are non-volatile. If, therefore, a mixture of mercuric sulphate and sodium chloride is heated together, double decomposition takes place and mercuric chloride passes away as vapour, condensing again on a cool surface.

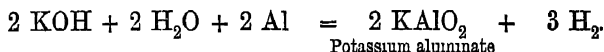


**Method 10. Interaction of Two Bases**—A few bases, notably the oxides and hydroxides of zinc, lead and aluminium, are soluble in caustic potash or caustic soda solution with formation of salts. The explanation is that, in the presence of a strong base such as caustic potash, a substance which generally acts as a weak base may act as a weak acid. The following equations represent the formation of salts in this manner:—



**Method 11. Interaction of Metals with Bases.**—A few metals also are soluble in potash solution with evolution of hydrogen, more especially zinc and aluminium. The salts obtained are the same as those produced when the oxides

or hydroxides of the metals are used instead of the metals themselves, as in the preceding method: thus when aluminium is dissolved potassium aluminate is formed—



Most metals are attacked slowly by fused potash, silver being the most resistant

**336 Double Salts**—These are complex salts formed by the union of two simple salts, *e. g.* a molecule of potassium sulphate,  $\text{K}_2\text{SO}_4$ , and one of aluminium sulphate,  $\text{Al}_2(\text{SO}_4)_3$ , together with 24 molecules of water, unite together to form a molecule of potassium aluminium sulphate or alum,  $\text{K}_2\text{SO}_4 + \text{Al}_2(\text{SO}_4)_3 + 24 \text{ H}_2\text{O}$ .

Double salts may be divided into two classes, according to their behaviour in solution. Some break up into the simple salts of which they are composed, and these then decompose further into ions in the usual way; thus alum breaks up into  $\text{K}_2\text{SO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$ , and these salts then yield the ions  $\text{K}$ ,  $\text{Al}$  and  $\text{SO}_4$ . Others do not decompose in this way, but ionise immediately, yielding a complex anion containing one of the metals; for example, potassium chloride,  $\text{KCl}$ , unites with platinum chloride,  $\text{PtCl}_4$ , to form the double salt  $2 \text{ KCl} + \text{PtCl}_4$  or  $\text{K}_2\text{PtCl}_6$ ; on dissolving this salt in water the kathions consist of  $\text{K}$  and the anions of the complex group  $\text{PtCl}_6$ . This salt may, therefore, be considered to be derived from the acid  $\text{H}_2\text{PtCl}_6$ , chloroplatinic acid, and is called potassium chloroplatinate.

Other examples of the first class of double salts are carnallite,  $\text{KCl} + \text{MgCl}_2 + 6 \text{ H}_2\text{O}$ , and ferrous ammonium sulphate,  $(\text{NH}_4)_2\text{SO}_4 + \text{FeSO}_4 + 6 \text{ H}_2\text{O}$ , and of the second class, potassium ferrocyanide,  $\text{K}_4\text{FeC}_6\text{N}_6$ , which yields the complex anion  $(\text{FeC}_6\text{N}_6)$ .

## QUESTIONS.—CHAPTER XXVI.

- 1 How is a *salt* defined in terms of the electrolytic theory?
2. Discuss the effect of mass on the nature of the products obtained by the action on metals of (1) the halogens, (2) nitric acid.
3. Why would you expect to get only the *lower* salt when a haloid acid acts on a metal which can give rise to two series of salts?
4. Why cannot anhydrous aluminium chloride be obtained by evaporating the aqueous solution of the salt to dryness? How is the anhydrous salt obtained?
5. Express by equations the action of (1) barium monoxide on sulphur trioxide, (2) zinc on silver nitrate, (3) caustic potash on ammonium sulphate, (4) caustic soda on zinc hydroxide.
- 6 Under what conditions can a salt be conveniently prepared by the interaction of two other salts?
7. Give examples of the formation of salts from (1) two bases, (2) a metal and a base.
- 8 What are double salts? Into what two classes can they be divided? Illustrate your answer by examples.



# CHAPTER XXVII.

## CHEMICAL CALCULATIONS.

337. **The Relations between Weight and Volume of Gases.**—From Avogadro's hypothesis it follows at once that the densities of gases are proportional to their molecular weights. In order to express the weight of any gas it is convenient to remember as the basis of calculation that 1 litre of hydrogen at the standard temperature ( $0^{\circ}$  C.) and pressure (760 mm. of mercury) weighs 0.09 gramme, or that 11.11 litres of hydrogen weigh one gramme.

If then we desire to ascertain the weight of any other gas under like conditions, we commence by expressing in chemical symbols the molecule of the gas thus—

The molecule of hydrogen is expressed by $H_2$ (2)		
"	"	nitrogen " $N_2$ (28)
"	"	oxygen " $O_2$ (32)
"	"	chlorine " $Cl_2$ (71)
"	"	ozone " $O_3$ (48)
"	"	phosphorus " $P_4$ (124)
"	"	water vapour " $H_2O$ (18)
"	"	hydrochloric acid " $HCl$ (36.5)
"	"	carbon dioxide " $CO_2$ (44)
"	"	nitric oxide " $NO$ (30)
"	"	sulphide dioxide " $SO_2$ (64)
"	"	sulphuretted } $H_2S$ (34)
		hydrogen }
"	"	ammonia " $NH_3$ (17)

and so on.

The relative weights are, then, those stated in parenthesis after the symbol in the above list, as derived from the respective atomic weights.

Thus the weight of a litre of nitrogen is 14 times that of a litre of hydrogen or  $(0.09 \times 14)$  grammes; a litre of carbon dioxide weighs  $(0.09 \times 22)$  grammes; a litre of sulphuretted hydrogen weighs  $(0.09 \times 17)$  grammes.

The alternative method of expressing the same facts is perhaps more readily applied in chemical calculations, viz. that 11.11 litres of hydrogen weigh 1 gramme or 22.22 litres of hydrogen weigh 2 grammes, the same number of grammes as that used for expressing the molecular weight. In this form the statement is quite general, that the molecular weight being  $m$ , 22.22 litres of any gas whatever weigh  $m$  grammes

22.22 litres of nitrogen	weigh 28 grammes.
22.22 " " oxygen	" 32 "
22.22 " " chlorine	" 71 "
22.22 " " sulphur dioxide	" 64 "
22.22 " " ammonia	" 17 "

It is convenient to remember both forms of the expression, as one or the other is more readily adapted for the purpose of calculation according to the terms which are given. For instance, if it be desired to calculate the weight of a certain volume of a gas, the former expression lends itself more readily for the purpose—as in the following example:—

(1) Required the weight of 100 c.c. of carbon dioxide at  $0^{\circ}$  C. and 760 mm. pressure—

1,000 c.c. (1 litre) of hydrogen	weigh 0.09 grammes.
" " carbon dioxide	" 1.98 "
100 cubic centimetres of " "	" 0.198 "

Should the weight of the gas be given, and its volume is to be determined, the second form of expression is more easily applied.

(2) Required the volume occupied by 0.5 gramme of ammonia at  $0^{\circ}$  C. and 760 mm. pressure—

17 grammes of ammonia occupy	22 22 litres.
1 gramme	„ occupies 1.307 „
0.5 „	„ „ 0.653 „

It is useful also to bear in mind that air is 14.435 times as heavy as hydrogen, since frequently the densities of vapours as actually determined by experiment are stated in terms of air as unit.

Thus the density of sulphur dioxide is found by experiment to be 2.247, air being the unit.

The density compared with hydrogen is therefore  $2.247 \times 14.435$ , or 32.43, a value agreeing well with that deduced from the accepted composition of this gas.

**338. Correction for Temperature and Pressure.**—We shall first consider the influence of variations of *temperature* on the volume of a gas, and consequently on the weight of a given volume.

We have seen (Chap. VIII) that a gas at  $0^{\circ}\text{C}$  expands  $\frac{1}{273}$  of its volume for each increment of one degree Centigrade in temperature. The more general form of expression, viz. that the volume of the gas is proportional to the absolute temperature (see § 49), will be found the most useful, as a few examples will show. In order to make the calculation it is, in the first place, necessary to convert the temperatures as ordinarily stated into absolute temperatures.

(3) A litre of gas is measured at  $0^{\circ}\text{C}$ ; what volume will it occupy at  $-20^{\circ}\text{C}$ ., and what at  $50^{\circ}\text{C}$ .?

$$\begin{aligned} 0^{\circ}\text{C} &= 273^{\circ}\text{ absolute.} \\ -20^{\circ}\text{C} &= 253^{\circ} \quad \text{„} \\ +50^{\circ}\text{C} &= 323^{\circ} \quad \text{„} \end{aligned}$$

$$\text{Volume required is at } -20^{\circ}\text{C. } 1 \text{ litre} \times \frac{253}{273} = 926.8 \text{ c.c.}$$

$$\text{„ „ „ } +50^{\circ}\text{C. } 1 \text{ litre} \times \frac{323}{273} = 1183.2 \text{ c.c.}$$

(4) The volume of a gas measured at  $10^{\circ}\text{C}$ . is found to be 150 c.c.; what volume would it occupy at the standard temperature ( $0^{\circ}\text{C}$ .)?

$$10^{\circ}\text{C} = 283^{\circ}\text{ absolute.}$$

Volume required is at  $0^{\circ}\text{C}$ .  $150 \times \frac{273}{283} = 144.7 \text{ c.c.}$

(5) The volume of a gas measured at  $15^{\circ}\text{C}$ . is found to be 250 c.c.; what volume would it occupy at  $-15^{\circ}\text{C}$ . and at  $57^{\circ}\text{C}$ . respectively?

$$\begin{aligned} 15^{\circ}\text{C} &= 288^{\circ} \text{ absolute.} \\ -15^{\circ}\text{C} &= 258^{\circ} \quad " \\ +57^{\circ}\text{C} &= 330^{\circ} \quad " \end{aligned}$$

Volume required at  $-15^{\circ}\text{C}$ .  $= 250 \times \frac{258}{288} = 224.0 \text{ c.c.}$

" " "  $+57^{\circ}\text{C}$ .  $= 250 \times \frac{330}{288} = 286.5 \text{ c.c.}$

And now let us consider the effect of variation in *pressure*. According to Boyle's Law (see § 50), the volume of a gas is inversely proportional to the pressure to which it is subjected when the temperature is constant.

(6) A gas measured at standard atmospheric pressure (760 mm) is found to occupy 1.5 litres; what volume will it occupy at 1,000 mm and at 100 mm. pressure?

Required volume at 1,000 mm. is  $1,500 \times \frac{760}{1,000} = 1,140 \text{ c.c.}$

" " " 100 mm. is  $1,500 \times \frac{760}{100} = 11,400 \text{ c.c.}$

(7) The volume of a gas at 500 mm. pressure is found to be 250 c.c.; what would it measure under 5 atmospheres pressure?

$$5 \text{ atmospheres} = (760 \times 5) \text{ mm.} = 3,800 \text{ mm.}$$

Required volume at 5 atmos.  $= 250 \times \frac{500}{3,800} = 32.9 \text{ c.c.}$

Finally, an example is given of the allowance for both temperature and pressure in the same expression.

(8) A gas occupies 190 c.c. at  $13^{\circ}\text{C}$ . and 740 mm. pressure; what volume would it occupy at standard temperature and pressure ( $0^{\circ}\text{C}$ . and 760 mm), and what at  $-13^{\circ}\text{C}$ . and 780 mm pressure?

13° C. = 286° absolute.

0° C. = 273° „

Volume at 0° C and 760 mm. =  $190 \times \frac{273 \times 740}{286 \times 760} = 176.6 \text{ c.c.}$

- 130° C. = 143 absolute.

Volume at - 130° C. and 780 mm. =  $190 \times \frac{143 \times 740}{286 \times 780} \text{ c.c.}$   
= 90.1 c.c.

**339. The Relation between Weight and Volume of Liquids.**—The specific gravity of liquids is expressed in terms of pure water at 15° C. as unit. The following table shows that the specific gravity of water varies at different temperatures, water at 4° being taken as 1 :—

Specific gravity of water at	0°	=	0.99987
„	2°	=	0.99997
„	4°	=	1.00000
„	10°	=	0.99975
„	15°	=	0.99916
„	20°	=	0.99826
„	25°	=	0.99712

In ascertaining the density of a liquid by comparison with water it is more convenient to make the determination at ordinary temperatures, and hence it is usual to adopt the specific gravity of water at 15° C. as the basis of comparison.

When we say that the specific gravity of a liquid is 1.8 we mean that it is heavier than water in the proportion 1.8 : 1 ; if therefore 1 c.c. of water weighs 1 gramme, 1 c.c. of such a liquid will weigh 1.8 grammes.\* The following examples will show how specific gravity of liquids enters into chemical problems.

\* This is not strictly accurate, since the gramme is the weight of 1 c.c. of water at 4° C. The correction, however, is only made in case a very exact expression is desired, and for ordinary purposes it is omitted. In any case the actual weight may be obtained by multiplying the result by 0.99916.

(9) What is the weight of 100 c.c. of sulphuric acid of sp. gr. 1.84?

100 c.c. of water	weighs 100 grammes.
" " sulphuric acid of the	} " 184 "
density given	

(10) Hydrochloric acid of sp. gr. 1.112 contains 21 per cent. by weight of gaseous hydrochloric acid, find the volume of hydrochloric acid gas in 10 c.c. of such acid.

By the method used in the previous problem 10 c.c. of hydrochloric acid will weigh 11.12 grammes.

$\frac{11.12 \times 21}{100} = 2.3352$  grammes, the weight of gaseous hydrochloric acid contained in it.

36.5 grammes of HCl. occupy 22.22 litres;  
 2.3352 grammes occupy  $\frac{22.22 \times 2.3352}{36.5}$  litres  
 = 1.421 litres.

**340. The Relation between Weight and Volume of Solids,** like that of liquids, is expressed in terms of water as unit. Thus, diamond is 3.5 times as heavy as water, and its sp. gr is 3.5; the sp. gr. of graphite is 2.2, of mercury 13.6.

The weight of these bodies that occupy the same volume as 1 gramme of water (that is, 1 c.c.) is 3.5, 2.2, and 13.6 grammes respectively.

This relation is seldom necessary in chemical calculations.

**341. Calculation of the Percentage Composition of a Body.**—When the chemical composition of a body is expressed by symbols, the proportions of the respective elements contained in it are the weights of the elements as determined from the table of atomic weights.

HCl indicates a compound formed by the union of 1 part by weight of hydrogen with 35.5 parts by weight of chlorine.

$\text{H}_2\text{O}$  indicates a compound formed by the union of 2 parts by weight of hydrogen with 16 parts by weight of oxygen.

$\text{CO}_2$  indicates a compound formed by the union of 12 parts by weight of carbon with 32 (*i.e.*  $2 \times 16$ ) parts by weight of oxygen

$\text{P}_2\text{O}_5$  indicates a compound formed by the union of 62 (*i.e.*  $2 \times 31$ ) parts by weight of phosphorus with 80 (*i.e.*  $5 \times 16$ ) parts by weight of oxygen

$\text{H}_3\text{PO}_4$  indicates a compound formed by the union of 3 parts by weight of hydrogen, 31 parts by weight of phosphorus, and 64 (*i.e.*  $4 \times 16$ ) parts by weight of oxygen.

36.5	parts by weight of	HCl	contain	1	pt	of	H	and	35.5	pts.	of	Cl		
18	"	"	"	2	pts.		H	and	16	"	"	O.		
44	"	"	"	12	"		C	and	32	"	"	O.		
142	"	"	"	62	"		P	and	80	"	"	O.		
98	"	"	"	3	"		H,	31	of	P	and	64	of	O.

The *percentage* composition is merely the statement of the relative weights of each of the constituents in 100 *parts* of the compound.

Thus, if 18 parts by weight of water contain 2 parts of hydrogen and 16 parts of oxygen, then 100 parts of water will contain—

$$\frac{2 \times 100}{18} \text{ parts of H, } i.e. 11.11;$$

$$\text{and } \frac{16 \times 100}{18} \text{ " " O, } i.e. 88.88;$$

and this represents the percentage composition of water.

(11) Find the percentage composition of potassium chlorate,  $\text{KClO}_3$ —

$$\begin{array}{rcl} \text{K} & = & 39.1 \\ \text{Cl} & = & 35.5 \\ \text{O}_3 & = & 48.0 \\ \hline & & 122.6 \end{array}$$

$$\begin{array}{rcl}
 \text{Percentage amount of K} & = & \frac{39.1 \times 100}{122.6} = 31.89 \\
 \text{,, ,, Cl} & = & \frac{35.5 \times 100}{122.6} = 28.95 \\
 \text{,, ,, O} & = & \frac{48 \times 100}{122.6} = \frac{39.16}{100.00}
 \end{array}$$

(12) Find the percentage amount of water of crystallisation in  $\text{FeSO}_4 + 7 \text{H}_2\text{O}$ .

$$\begin{array}{rcl}
 \text{Fe} & = & 56 \\
 \text{S} & = & 32 \\
 \text{O}_4 & = & 64 \\
 7 \text{H}_2\text{O} & = & 126 \\
 \hline
 & & 278
 \end{array}$$

278 parts of  $\text{FeSO}_4 + 7 \text{H}_2\text{O}$  contain 126 parts of water.

$$\text{Percentage of water} = \frac{126 \times 100}{278} = 45.32.$$

**342. Determination of the Formula of Substance.**—The question which even more frequently arises in practice is the converse one, the determination of the formula of a substance from the results of analysis of the substance. We have seen already that the relative composition by weight of a body is obtained by taking the atomic weight of each constituent, and where more than one atom of any constituent is present, then the multiple of that according to the number of atoms.

*E.g.*, for  $\text{COCl}_2$ —

	Atomic weight.	No of atoms.	Product.	Percentage composition.
C	12	1	12	12.12
O	16	1	16	16.16
Cl <sub>2</sub>	35.5	2	71	71.72

We now reverse the process, and desire to determine the relative number of atoms of each element, having



given the composition by weight of a body as deduced from its analysis—

$$\begin{aligned} \text{S} &= 23.7 \text{ per cent.} \\ \text{O} &= 23.7 \quad \text{,,} \quad \text{,,} \\ \text{Cl} &= 52.6 \quad \text{,,} \quad \text{,,} \end{aligned}$$

Let  $n$ ,  $n'$ ,  $n''$  be the number of atoms of S, O, and Cl respectively, the atomic weights being 32, 16, and 35.5; we have the relative weights of each of the constituents—

$$32 n, 16 n', \text{ and } 35.5 n''.$$

These values are proportional to the weights as represented by the percentage composition, viz.—

$$23.7, 23.7, 52.6.$$

Thus—

$$\begin{aligned} 32 n &\propto 23.7 \text{ and } n \text{ is proportional to } 0.74. \\ 16 n' &\propto 23.7 \quad \text{,,} \quad n' \quad \text{,,} \quad \text{,,} \quad 1.48. \\ 35.5 n'' &\propto 52.6 \quad \text{,,} \quad n'' \quad \text{,,} \quad \text{,,} \quad 1.48. \end{aligned}$$

The *simplest proportion in whole numbers* is—

$$1 : 2 : 2,$$

and the formula on this assumption is—



This, then, is the *empirical formula* as deduced solely from the consideration of the results of the analysis. It is quite consistent with such a calculation that the formula should be  $\text{S}_2\text{O}_4\text{Cl}_4$ , or  $\text{S}_3\text{O}_6\text{Cl}_6$ , or any such multiple. Which of these is to be finally accepted can only be decided after a determination of the vapour density of the body, or of its chemical constitution and character, and this would be the *molecular formula* of the body.

To determine the empirical formula of a body, we therefore divide the results of analysis by the respective atomic weights, and the numbers so obtained are *proportional* to the number of atoms.

(13) The percentage composition of a compound is found to be H = 5.88 and O = 94.12 find its formula

In this case  $n$  and  $n'$  being in proportion to the number of atoms of hydrogen and oxygen respectively

$$n\text{H} = 5.88, \text{ and H being 1, } n = 5.88;$$

$$n'\text{O} = 94.12, \text{ and O being 16, } n' = 5.88.$$

The body, therefore, consists of an equal number of atoms of H and O, and the simplest formula would be HO. Chemical considerations, however, compel us to accept a multiple of this, viz  $\text{H}_2\text{O}_2$ , as the formula of hydrogen peroxide, the substance which has this composition.

(14) Find the formula of a substance having the composition—

$$\text{Mg} = 9.76.$$

$$\text{S} = 13.01.$$

$$\text{O} = 26.01.$$

$$\text{Water of crystallisation} = 51.22.$$

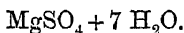
$$\text{Mg gives } \frac{9.76}{24} = 0.406 \text{ as proportional number.}$$

$$\text{S} \quad \text{,,} \quad \frac{13.01}{32} = 0.406 \quad \text{,,} \quad \text{,,}$$

$$\text{O} \quad \text{,,} \quad \frac{26.01}{16} = 1.626 \quad \text{,,} \quad \text{,,}$$

$$\text{H}_2\text{O} \quad \text{,,} \quad \frac{51.22}{18} = 2.846 \quad \text{,,} \quad \text{,,}$$

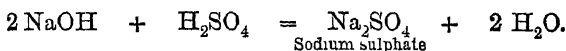
From these numbers we deduce as the simplest whole numbers bearing the same relation to one another 1 : 1 : 4 : 7, and the simplest formula for the body is—



**343. Application to Chemical Problems.**—We have now considered the fundamental calculations which enter into chemical problems, and a few examples will be given to show how these bear upon questions involving chemical decomposition and interchange.

(15) What weight of caustic soda (NaOH) will be needed to just neutralise 10 c.c. of dilute sulphuric acid (sp. gr. 1.155) containing 21 per cent. of  $\text{H}_2\text{SO}_4$ ?

In all cases where a chemical reaction is concerned, involving considerations of weight or volume, it is well to state the reaction in the form of an equation at the outset—



From this we see that 2 NaOH neutralise  $\text{H}_2\text{SO}_4$ , the respective weight relations being—

$$2 (23 + 16 + 1) \text{ and } (2 + 32 + 64) \text{ or } 80 : 98.$$

80 parts by weight of caustic soda serve to neutralise 98 parts by weight of sulphuric acid.

Now determine the actual weight of sulphuric acid that is to be neutralised—

10 c.c. of the dilute sulphuric acid (sp. gr. 1.155) weigh 11.55 grms.

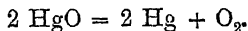
21 per cent. of this is  $\text{H}_2\text{SO}_4$ , i.e.  $\frac{11.55 \times 21}{100} = 2.4255$  grms.

Required amount of caustic soda is—

$$\frac{2.4255 \times 80}{98} \text{ grammes, or } 1.98 \text{ grammes.}$$

(16) What volume of oxygen collected at standard temperature and pressure ( $0^\circ$  and 760 mm.) is given off on heating 10 grammes of mercuric oxide?

The equation representing the action of heat on mercuric oxide is—



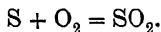
First determine the *weight* of oxygen from the above equation, which shows that 432 parts of mercuric oxide yield 32 parts of oxygen, or, in simpler numbers, 27 parts yield 2 parts of oxygen.

10 grammes therefore yield  $\frac{2 \times 10}{27}$ , or 0.74 grammes.

Now 32 grammes of oxygen occupy at standard temperature and pressure 22.22 litres, and the *volume* of oxygen corresponding to this weight is—

$$\frac{0.74 \times 22.22}{32} = 514 \text{ cubic centimetres.}$$

(17) What weight of sulphur must be burnt so as to yield 1 litre of sulphur dioxide at standard temperature and pressure?



Here we start from a known *volume* of gas and must work back to the *weight* in terms of which the result is to be expressed.

22.22 litres of  $\text{SO}_2$  weigh 64 grammes.

1 litre of  $\text{SO}_2$  weighs  $\frac{64}{22.22}$  or 2.869 grammes.

Also 64 grammes of  $\text{SO}_2$  contain 32 grammes of S,  
 and 2.869 " "  $\text{SO}_2$  " " 1.4345 " S  
 1.4345 grammes of sulphur will therefore be required to produce 1 litre of  $\text{SO}_2$ .

Such a calculation may, however, be shortened by the consideration that as 32 grammes of sulphur, according to the equation, yield 64 grammes or 22.22 litres of  $\text{SO}_2$ ,

$$\frac{32}{22.22} \text{ grammes will yield 1 litre of } \text{SO}_2.$$

The next example will be rendered more complex by introducing conditions of temperature and pressure differing from the standard. No further difficulty is really involved, except that the correction for temperature and pressure must be made.

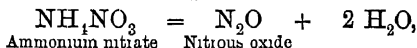
(18)  $2\frac{1}{2}$  litres of nitrous oxide have been collected at  $39^\circ \text{C}$  and 741 mm. pressure; what weight of ammonium nitrate has been decomposed in order to supply the gas?

First eliminate the irregularity introduced by the temperature and pressure, by determining what volume the

gas would have occupied had it been collected at standard temperature and pressure. This will be—

$$\frac{2.5 \times 273 \times 741}{312 \times 760} \text{ litres, or } 2.133 \text{ litres.}$$

Now according to the equation—



80 grammes of ammonium nitrate yield 44 grammes (or 22.22 litres) of nitrous oxide, and hence

$$\frac{80 \times 2.133}{22.22} \text{ grammes, or } 7.681 \text{ grammes, of ammonium}$$

nitrate have been decomposed.

(19) One gramme of water is (a) converted into steam at 100° C., (b) decomposed by means of sodium and the hydrogen collected at 13° C., what volume will each occupy, the barometer at the time standing at 750 mm. ?

First, let us consider the case of the steam. This being water vapour has, at standard temperature and pressure, a density such that, as previously shown,

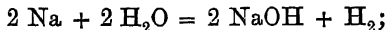
18 grammes is the weight of 22.22 litres.

Thus 1 gramme occupies  $\frac{22.22}{18}$  or 1.234 litres.

At 100° C. and 750 mm. pressure this occupies—

$$\frac{1.234 \times 373 \times 760}{273 \times 750} = 1.71 \text{ litres.}$$

Secondly, as to the hydrogen, the decomposition is represented by the equation—



from which we see that 36 grammes of water yield 2 grammes of hydrogen, and therefore 1 gramme of water yields  $\frac{1}{18}$  gramme of hydrogen.

The volume of hydrogen at standard temperature and pressure is thus  $\frac{1111}{18}$  or 0.62 litre. Corrected so as to

represent the volume at 13° C. and 750 mm. pressure this becomes—

$$\frac{0.62 \times 286 \times 760}{273 \times 750} = 0.658 \text{ litre.}$$

The whole of the more important elements entering into the treatment of chemical problems have now been discussed, and it only remains to add some examples in further illustration of their application to chemical reactions.

(20) 10 grammes of mercury are heated with excess of concentrated sulphuric acid and the sulphur dioxide formed is collected at 15° C and 765 mm. pressure; what volume does it occupy?

Here, as in most cases, it is best to commence by a statement of the reaction which takes place.



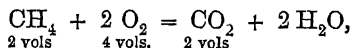
200 grammes of mercury give 64 grammes of  $\text{SO}_2$ ,  
 or 200   "               "               "   22.22 litres of  $\text{SO}_2$   
 $\therefore$  10   "               "               "   1.111   "   "  
 at standard temperature and pressure.

Volume at 15° C. and 765 mm pressure is then

$$\frac{1.111 \times 288 \times 760}{273 \times 765} = 1.164 \text{ litre.}$$

(21) 25 c.c. of marsh gas ( $\text{CH}_4$ ) are mixed with 500 c.c. of air and exploded in a eudiometer; what volume of gas should there be (a) before the removal of the carbon dioxide formed, (b) after the absorption of the carbon dioxide by means of caustic potash? The temperature and pressure may be assumed to be the same when each of the readings of volume were taken.

The chemical reaction which takes place is



the nitrogen of the air taking no part in the combustion.

It is further manifest on inspection that the 2 volumes of marsh gas and 4 volumes of oxygen, before explosion, give

rise to 2 volumes of carbon dioxide, the space occupied by the water being negligible.

Thus 6 volumes are reduced to 2, and the diminution is 4 volumes.

But the marsh gas occupies 25 c.c., and is represented by 2 volumes

The diminution in volume is therefore 50 c.c., and the 525 c.c. of mixed gases originally present in the eudiometer have been reduced to 475 c.c.

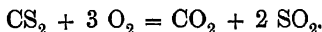
Similarly the  $\text{CO}_2$  occupies the same volume as the marsh gas from which it was obtained, and is thus 25 c.c., and if this be removed there will remain 450 c.c. of gas in the eudiometer. The result is that the residual gas—

- (a) before removal of  $\text{CO}_2$  is 475 c.c.  
 (b) after        "       "       "       450 c.c

(22) 10 c.c. of liquid carbon bisulphide (sp. gr. 2.63) are burnt in oxygen; find the volume of the resulting gases measured at standard temperature and pressure.

We must first ascertain the weight of the carbon bisulphide. Its sp. gr. being 2.63, the 10 c.c. will weigh 26.3 grammes.

The chemical change during combustion is represented in the equation—



76 grammes of  $\text{CS}_2$  yield 44 grammes or 22.22 litres  $\text{CO}_2$ .  
 "       "       "       "       128       "       "       44.44       "        $\text{SO}_2$ .  
 "       "       "       "       66.66 litres of  $\text{CO}_2$  and  $\text{SO}_2$   
 together.

26.3 grammes of  $\text{CS}_2$  yield  $\frac{66.66 \times 26.3}{76} = 23.08$  litres.

(23) Considering air as a mixture of 79 per cent. by volume of nitrogen with 21 per cent. by volume of oxygen (*i. e.* neglecting argon), find the density of air compared with hydrogen. Also find the density of the vapour of carbon bisulphide compared with air.

79 vols. of nitrogen are as heavy as  $79 \times 14$ , or 1,106 vols. of H

21 vols of oxygen are as heavy as  $21 \times 16$ , or 336 vols. of H

100 vols. of air are as heavy as... ..  $\overline{1,442}$  vols. of H.

$\therefore$  Density of air is 14.42.\*

Density of the vapour of bisulphide of carbon is  $\frac{12 + 64}{2}$

or 38, compared with hydrogen.

Compared with air it is therefore  $\frac{38}{14.42} = 2.635$ .

### Atomic Weights to be used in the Following Calculations.

Hydrogen,	1.	Chlorine,	35.5.
Carbon,	12.	Potassium,	39.
Nitrogen	14.	Calcium,	40.
Oxygen,	16.	Iron,	56.
Sodium,	23.	Bromine,	80.
Magnesium,	24.	Silver,	107.6
Phosphorus,	31.	Antimony,	119.6.
Sulphur,	32.	Mercury,	200.
Lead, 206.4.			

### QUESTIONS.—CHAPTER XXVII.

1. The volume of a permanent gas at  $0^{\circ}\text{C.}$  is 3 litres; at what temperature would it occupy 4 litres, the pressure remaining unaltered?
2. Two samples of gas occupy the same volume, but one is at  $-20^{\circ}\text{C.}$ , and the other at  $20^{\circ}\text{C.}$ ; what is their relative volume when both are at  $0^{\circ}\text{C.}$ ?

\* Actual density at normal composition is taken as 14.435.



3. The volume of a gas at  $13^{\circ}\text{C}$ . is 100 c.c.; find its volume at  $-130^{\circ}\text{C}$ ., at  $-13^{\circ}\text{C}$ ., and at  $130^{\circ}\text{C}$ .
4. A gas under standard atmospheric pressure measures 209 c.c., what volume will it occupy under a pressure of  $\frac{1}{10}$ ,  $\frac{1}{2}$ , 2 and  $5\frac{1}{2}$  atmospheres respectively?
5. What volume will half a litre of gas measured at 750 mm. pressure occupy when subjected to a pressure of 850 mm. of mercury?
6. A rectangular vessel 10 c.m. long, 5 c.m. wide, and 3.5 c.m. deep, is filled with gas at  $100^{\circ}\text{C}$ . and 770 mm pressure; what volume will the gas occupy at standard temperature and pressure?
7. A sample of gas is collected in a eudiometer, and it is found that the level of the mercury in the eudiometer is 257 mm. above that in the trough; also the height of the barometer at the time is 745 mm. under what pressure is the gas?
8. A sample of gas is collected at standard temperature and pressure, and the pressure is then doubled and the temperature gradually raised until the volume of the gas is the same as it was originally; at what temperature does this occur?
9. Under how many atmospheres pressure will steam have the same density as water (1 c.c. weighs one gramme), if the contraction takes place in accordance with Boyle's law, and the temperature remains at  $600^{\circ}\text{C}$ .?
10. If the temperature remains at zero, at what pressure will hydrogen have a density equal to 0.62 of that of water, this being the density found by Dewar for hydrogenium?
11. One cubic centimetre of bromine (density 3.2) is transformed into vapour at  $78^{\circ}\text{C}$ .; determine the volume occupied by the vapour.
12. The sp. gr. of pure nitric acid being 1.522, find the weight of 100 c.c. of it, and the volume that you must take to weigh 100 grammes.
13. What volume of such acid will be required to just neutralise 100 grammes of caustic potash (KOH), and what weight of potassium nitrate is formed?

14. Calculate the percentage composition of calcium carbonate, what percentage of carbon dioxide does it contain?
15. Chlorine forms with water a solid hydrate, having the composition  $\text{Cl}_2 \cdot 8 \text{H}_2\text{O}$ ; calculate the percentage of hydrogen, chlorine, and oxygen contained in this body.
16. Find the empirical formula of a compound consisting of 46.66 per cent of iron and 53.33 per cent. of sulphur.
17. An oxide of iron contains 72.3 per cent. of iron; determine its empirical formula.
18. Determine the simplest formula for a salt having the following percentage composition:—

Sodium,	29.36
Phosphorus,	26.38
Oxygen,	44.26
	<hr/> 100.00

19. A solution of caustic soda having the sp. gr. 1.32 contains 28.8 per cent. of  $\text{NaOH}$ ; what weight of sulphuric acid is required to be just sufficient to neutralise a litre of such a solution?
20. What volume of sulphuretted hydrogen at  $13^\circ \text{C}$ . and 798 mm. pressure is required to effect the complete precipitation of one gramme of corrosive sublimate,  $\text{HgCl}_2$ ?
21. What weight of pure antimony sulphide,  $\text{Sb}_2\text{S}_3$ , should yield a litre of sulphuretted hydrogen collected at  $10^\circ \text{C}$ . and 760 mm pressure?
22. Determine the volume of chlorine required to convert 10 grammes of phosphorus into the pentachloride.
23. A gramme of common salt is dissolved in water and excess of silver nitrate solution is added; what weight of silver chloride should be precipitated?
24. Calculate (a) the volume, (b) the weight, of carbon dioxide in the air of a room 6 mètres long, 4 mètres wide, and 3 mètres high, if there is 1 volume of this gas present per 1,000 volumes of the air.

25. Dumas determined the relative amounts of nitrogen and oxygen in air by passing it over heated copper. He found—

Weight of tube and copper before experiment,	120	grms
" " " " " after	121 15	"
" " globe when exhausted . . .	852	"
" " " and nitrogen . . .	855.85	"

From these numbers calculate the percentage composition of air by weight, and deduce its percentage composition by volume

26. Dumas determined the composition of water synthetically by passing hydrogen over heated copper oxide, and found—

Weight of tube and copper oxide before experiment,	334 598	grs.
" " " " " after	314 236	"
" " drying tubes before experiment . .	426 358	"
" " " " after	449 263	"

Calculate the percentage composition of water by weight

27. Ten grammes of steam are passed over red-hot iron; what volume of hydrogen at  $26^{\circ}$  C. and 741 mm. pressure will be obtained if one-third of the steam undergoes decomposition?
28. Fifteen cubic centimetres of ammonia are completely decomposed by electric sparks, and then 40 c.c. of oxygen are added and the mixed gases exploded; state the gases present and the volume of each (*a*) just before exploding, (*b*) after exploding.
29. A mixture of ten litres of oxygen with one litre of carbon dioxide is shaken up with 100 c.c. of water; determine the volume of each gas that will be dissolved—the barometer at the time standing at 760 mm. and the thermometer at zero
30. Make the same determination with a mixture of one litre of oxygen and 10 litres of carbon dioxide.
31. A litre of sea-water (sp gr. 1.03) is evaporated to dryness, and found to leave as residue 36.4 grammes

- of salts; find the percentage of solid matter in the sea-water.
32. Given that a mètre is equivalent to 39.37 inches, calculate the number of cubic inches in a litre, and the number of litres in a cubic foot.
33. Determine the percentage of carbon in cane-sugar ( $C_{12}H_{22}O_{11}$ ) and the volume of carbon dioxide that results from the combustion of 0.2 gramme of sugar.
34. A mixture of 20 c.c. of ethylene and 200 c.c. of oxygen is exploded in a eudiometer; what volume of gas remains after the explosion, and what volume when the carbon dioxide is subsequently removed by absorption with potash?
35. What quantity of crystallised oxalic acid ( $C_2H_2O_4 + 2H_2O$ ), heated with excess of sulphuric acid, will yield 5 litres of gas at standard temperature and pressure?
36. If 50 c.c. of sulphuretted hydrogen be mixed with excess of chlorine, what volume of hydrochloric acid will be formed, and what weight of sulphur liberated?
37. A gramme of a substance containing carbon is heated with lead oxide, and found to form 10 grammes of metallic lead; what percentage of carbon was present?
38. What weight of iron must be dissolved in dilute sulphuric acid in order to yield sufficient hydrogen to fill a balloon having a capacity of 100 cubic mètres?
39. Ten grammes of carbon are burnt in 1,000 litres of air (taken as consisting of 79 vols. of N and 21 of O) at  $15^\circ$  C. and 700 mm. pressure; find the percentage of nitrogen, oxygen, and carbon dioxide in the air after the combustion is complete.

## SECTION III.—THE CHEMISTRY OF DAILY LIFE.

### CHAPTER XXVIII.

#### COMMON METALS AND ALLOYS.

344. Iron is the most important of all the metals. It has been found in the *metallic* state in Greenland and other parts of the world, and especially in meteorites, some of which consist almost wholly of iron and nickel. It occurs chiefly, however, in the form of oxides, carbonate and sulphide. The most important British ore is *clay ironstone*, an earthy form of ferrous carbonate; in Scotland the clay ironstone is generally mixed with carbonaceous matter and is called *black band ironstone*. In extracting the metal these ores are first calcined to drive off carbon dioxide, moisture and sulphur. The residue, which consists of ferric oxide and earthy matter, is introduced into a *blast furnace* together with coke and limestone. At the high temperature of the furnace the coke as well as carbon monoxide produced from it reduces the oxide of iron to the metallic state, and the molten metal is periodically run off into moulds consisting of a network of channels formed in sand. The bars of iron so obtained are called *pigs*

Iron, as produced in the blast furnace, is known as *cast-iron*, and contains a number of impurities, the chief

of which is carbon. To obtain pure iron from cast-iron, the latter is melted in a current of air and stirred about (*puddled*), whereby the impurities are oxidised, carbon passing away as carbon dioxide. The product is called *wrought-iron*.

Cast-iron is converted into *steel* by introducing the molten metal into a large pear-shaped steel vessel (called a *converter*) lined with suitable material to withstand the high temperature, and blowing air through till the impurities are oxidised. A quantity of carbon (in the form of *ferro-manganese* or *spiegel-eisen*, an alloy of iron and manganese containing about 6 per cent. of carbon) is now added, which is considerably less than that originally present in the cast-iron.

The properties of wrought-iron, cast-iron and steel differ considerably. This difference depends chiefly upon the quantity of carbon present. Wrought-iron, which is nearly pure iron, is a soft, grey, malleable metal possessing considerable tensile strength (*i.e.* a heavy weight can be hung on to a tolerably thin iron wire without breaking it). As the percentage of carbon increases, the iron becomes harder and less malleable, up to a certain point the tensile strength increases, but beyond this it diminishes. Cast-iron, which contains the highest percentage of carbon, is very brittle, and its tensile strength is much smaller than that of wrought-iron. Steel is very tough, possessing even greater tenacity than wrought-iron, and it possesses the remarkable property of becoming very hard on being heated up and then suddenly cooled. If it is now heated again to a moderate temperature, it becomes softer, and by varying the temperature the hardness can be regulated. This process is called "tempering," and the steel is said to "take a temper"; wrought-iron and cast-iron cannot be tempered.

**Uses** — *Wrought-iron* was formerly used for a great variety of purposes, but steel has now taken its place to a very large extent. The greater part of the wrought-iron manufactured at the present time is employed for

making the cores of electromagnets used in dynamos and electric motors. A considerable amount is also employed by the blacksmith, who requires a metal which can be easily worked at a red heat; horse-shoes, for instance, are made of wrought-iron.

*Cast-iron* is, as its name implies, used for *castings*—e. g. fire-grates, fly-wheels and pistons; its value for this purpose depends upon (1) its low melting-point compared with wrought-iron and steel, (2) the fact that on cooling from a temperature somewhat above the melting-point a considerable expansion takes place which enables the molten metal to fill every part of a mould into which it is poured.

The purposes for which *steel* is employed are innumerable; it is used for making tools, guns, armour-plating for ships, boiler-plates, rails, girders for bridges, etc. etc. Pure iron melts at about  $2000^{\circ}\text{C}$ ., cast-iron at about  $1600^{\circ}\text{C}$ . The melting-point of pure iron is therefore about  $1000^{\circ}\text{C}$ . higher than that of copper. We should regard iron then as a metal with an extremely high melting-point.

All the forms of iron (wrought-iron, cast-iron and steel) if exposed to moist air become coated with the hydroxide of the metal (iron rust). Pure dry air has no effect at ordinary temperatures upon iron. The metal is readily attacked by even very dilute mineral acids, and in this respect resembles zinc.

**345. Copper** is a metal which appears red by reflected light, but extremely thin plates of it transmit green light. Its specific gravity is 8.95; it possesses the properties of toughness and malleability to a high degree, and is the second best conductor of heat and electricity known. On this last property depends its use in the manufacture of electric cables. Dry air is without action on copper at ordinary temperatures, but in presence of moisture and carbon dioxide it becomes corroded and coated with a deposit of green basic carbonate (verdigris). Copper is largely employed in making domestic utensils, and

electric batteries, as well as in electro-plating and electro-typing.

The alloys of copper are of great importance. The chief are *brass* (copper and zinc); *bronze*, *gun-metal*, *speculum metal* and *bell metal* (copper and tin); *German silver* or *nickel silver* (copper, nickel and zinc); aluminium bronze (copper and aluminium); gold coinage (gold and copper); and silver coinage (silver and copper). These alloys are considered respectively under the elements other than copper. *Dutch metal* used as a cheap substitute for gold-leaf, contains a little zinc.

Copper melts at  $1080^{\circ}\text{C}$ . It is therefore not easy to melt copper, but thin wire, or foil, may be fused in the hottest parts of the Bunsen flame.

Copper is attacked by even very dilute nitric acid, but dilute hydrochloric and sulphuric acids have very little action upon it.

**346. Lead** is a soft, bluish-grey metal with a bright lustre at a freshly cut surface, it tarnishes in air and is superficially acted upon by water containing dissolved air, especially in presence of carbon dioxide or in water containing certain salts in solution. This behaviour of lead towards water is of extreme importance, since drinking water is always conveyed, for some distance at any rate, through leaden pipes, so that there is always the possibility of contamination of the water unless proper precautions are taken. The lead oxide which may be formed is itself slightly soluble in water, whilst the carbonate which is also a possible product is soluble in water containing carbon dioxide. Thus we may get drinking water containing poisonous lead compounds. If however the water is "permanently" hard (see § 114) a protective layer of lead sulphate will form, and the further solvent action of the water be thus prevented. In its behaviour towards the common mineral acids lead is very similar to copper. It is very malleable but possesses little tenacity; its specific gravity is 11.38, and it melts at  $327^{\circ}\text{C}$ . The softness and malleability of lead



and its low melting-point render it of great value in the arts. It is, for instance, used in making piping and rifle-bullets, the metal being heated and forced through perforations of the required shape.

Lead forms several useful alloys. *Type metal* consists of two parts of lead, one part of antimony, and one of tin; *common pewter* and *solder* will be referred to under "tin."

347. **Zinc** is a white metal with a bluish tinge, and melts at  $419^{\circ}$  C. It is brittle at ordinary temperatures, but at about  $100^{\circ}$ – $150^{\circ}$  C. it becomes ductile and may be drawn into wire and rolled into sheet; above  $200^{\circ}$  C. it loses its cohesion and may be readily powdered. Zinc is only very slightly acted upon by air at ordinary temperatures. On this account it is used for *galvanising* iron, this consists in coating iron with a thin layer of zinc by dipping it in the melted metal. Zinc is also used in electric batteries, in the *Parkes process* for desilverising lead and in the extraction of gold, to precipitate the metal from its solution in potassium cyanide. *Zinc dust* obtained in the extraction of the metal consists of a mixture of the metal and the oxide. It is used as a reducing agent in Organic Chemistry.

Zinc forms a number of important alloys with copper, the chief of which are *brass* and *Muntz's metal*. These alloys are harder than copper; they are malleable and will take a high polish. *Brass* contains one part of zinc to two of copper; it is very extensively used in the arts: *Muntz's metal* is composed of three parts of copper, two parts of zinc and a little lead; it is used for sheathing ships. Commercial zinc is easily attacked by the common mineral acids, so that vessels of zinc, or of galvanised iron, should not be brought into contact with these liquids.

348. **Tin** is a white malleable metal melting at  $230^{\circ}$  C. It is unacted upon by air at ordinary temperatures. Tin finds many uses in the arts. Vessels made of iron, copper and brass are very frequently "tinned"—i. e. coated with a protective layer of tin. *Tin plate* is tinned iron, and is made by placing sheets of iron, which have

been carefully cleaned with dilute sulphuric acid and subsequent rubbing with sand and water, in melted tallow and then in melted tin. The tin forms an alloy with the iron and so adheres to it. The plate is now dipped into a second bath of melted tin which gives it a coating of pure tin over the alloy. "Tins" are usually made of tinned iron. In tinning copper or brass the vessel is first cleaned by heating it and rubbing with sal-ammoniac, melted tin is then poured over it and forms an alloy as in the case of iron. Many vessels used for technical and domestic purposes are made of tin plate, and the metal is an essential constituent of a number of important alloys. *Common pewter* and *solder* consist of tin and lead. Pewter contains about three parts of tin to one of lead, solder has a variable composition, but contains less tin than pewter. *Gun-metal* is composed of nine parts of copper and one part of tin; *speculum metal* contains two parts of copper and one of tin; it is capable of taking a very high polish, and is used for making the specula of reflecting telescopes. *Bronze* is a tough hard alloy consisting of copper and tin and small quantities of other metals; *bronze canon* contains 95 parts of copper, four parts of tin and one of zinc. *Bell metal* contains from three to five parts of copper to one of tin, it is hard and very sonorous; to this last property it owes its special value for bell-making. *Phosphor bronze* contains a small quantity of phosphorus in addition to tin and copper: this renders it very hard and tough, and it is largely used in making machinery. For *tin amalgam* see § 351.

Tin may be rolled into very thin sheets, and in this form constitutes the well-known "tin foil." Tin, like zinc, is acted upon by hydrochloric acid but not so easily. Nitric acid attacks it readily, but *dilute* sulphuric acid has little action upon it.

349. **Silver** is a white lustrous metal capable of taking a high polish. It is very malleable and ductile, and is the best conductor of heat and electricity known. Its

specific gravity is about 10.5. It melts at  $960^{\circ}\text{C}$ . It is not attacked by pure air, but gradually tarnishes in towns owing to the presence in the atmosphere of compounds of sulphur which convert it into black silver sulphide.

Silver readily forms alloys with other metals. Those with copper are largely used in the arts in place of pure silver, which is too soft for most purposes such as jewellery and coinage. The addition of a small quantity of copper renders silver harder, tougher and more fusible. English silver coinage contains 75 per cent of copper, that of France, Germany and Austria contains 10 per cent. of copper. An alloy of silver and nickel is used for coinage in Switzerland. Silver is also used for *silvering*, *plating* and *electro-plating* other metals and for *silvering* glass.

350. Gold is a yellow metal characterised by great malleability and ductility. Its specific gravity is 19.5, so that it is almost *twice* as heavy, bulk for bulk, as lead. Its melting-point,  $1062^{\circ}\text{C}$ ., is very near that of copper; it should be possible, therefore, to melt thin gold wire in the Bunsen flame. It is unacted upon by air at any temperature, and is not attacked by any single mineral acid, and its frequent occurrence in the free state in nature is to be explained by these facts. It dissolves quite readily, however, in *aqua regia*, which is a mixture of nitric and hydrochloric acids, and yields the chloride.

Pure gold is too soft for making jewellery or coinage. This difficulty is overcome by alloying it with a small proportion of copper or silver, copper darkens the colour whilst silver renders it lighter. English gold coinage consists of 22 parts of gold to two parts of copper; American, German and Italian gold coins contain nine parts of gold to one of copper. Trinket gold contains both copper and silver. Besides being used for jewellery and coinage, gold is employed extensively for electro-plating, and, in the form of gold-leaf, for gilding purposes. No

other metal is capable of being hammered into such thin sheets as gold is, and none is more ductile.

351. **Quicksilver** (Mercury) is a silver-white metal with a high specific gravity (13.596), and is the only metal which is liquid at the ordinary temperature. It becomes solid at  $-40^{\circ}\text{C}$ . It forms alloys with many metals, some of which are of great practical value. These alloys are called *amalgams*. The most important amalgams are :— *sodium amalgam*, which serves as a convenient reducing agent (more especially in Organic Chemistry) ; *tin amalgam* used for coating the backs of mirrors ; *cadmium amalgam* and *tin-silver amalgam* used for stopping teeth. Mercury is much used in the extraction of gold and silver from their ores owing to its power of amalgamating with these metals ; it is also employed in making physical and chemical apparatus and in preparing the compounds of the metal several of which are used medicinally. Grey mercurial ointment is made by rubbing up mercury and fat together till the mercury is broken up into very minute globules which are scattered through the mass.

352. **Aluminium** is a white metal which like zinc also shows a bluish tinge. Its specific gravity is low (2.6). It possesses great tensile strength and malleability, and is unacted upon by air at any ordinary temperature. These properties render it specially suitable for a variety of purposes. It is used, for example, for making cooking utensils, balance-beams and chemical weights. Aluminium forms some important alloys. *Aluminium bronze*, consisting of 90 per cent. of copper and 10 per cent. of aluminium, possesses great tensile strength and takes a high polish. It is golden-yellow in colour and is used in making jewellery and scientific instruments. An alloy of aluminium containing 10 per cent. of tin closely resembles brass, but is lighter and less easily corroded. Aluminium melts at  $654^{\circ}\text{C}$ . Hydrochloric and sulphuric acids dissolve aluminium with evolution of hydrogen, but neither dilute nor concen-

trated nitric acid produces much effect. It dissolves easily in the alkalis, and decomposes water at 100° C.

**353 Sodium** is a soft, malleable metal of specific gravity 0.974, and melts at 95.6° C., it possesses a silvery lustre when freshly cut, but rapidly tarnishes through oxidation even at ordinary temperatures. Sodium is a strong reducing agent, and is on this account used in the extraction of certain elements, *e.g.* magnesium, silicon and boron from their oxides. It is also used in the manufacture of sodium peroxide and of cyanides. With mercury, sodium forms an important amalgam. (See § 351.)

Sodium decomposes water at the ordinary temperature, liberating hydrogen and producing sodium hydroxide.

**354. Magnesium** is a bright white metal of low specific gravity (1.75). It melts at 633° C, that is to say below a dull red heat. It decomposes steam with liberation of hydrogen and formation of magnesia. Magnesium burns very brightly in air, forming a mixture of magnesia and magnesium nitride. This property of uniting directly with nitrogen is shared only by a few other metals. The light emitted by burning magnesium is made use of in pyrotechny, in signalling and (on account of its richness in chemically active or "actinic" rays) in photography. Magnesium in the form of powder acts as a powerful reducing agent, and is used in the extraction of some elements, *e.g.* silicon and boron, from their oxides.

**355. Platinum** is a metal which though not common in the ordinary sense is very interesting, and to the chemist at any rate exceedingly useful. In colour it resembles tin, is as soft as copper, and next to gold and silver, is the most malleable of metals. It can be welded like iron at a white heat, and like this metal has an extremely high melting-point, namely, about 2000° C. It can be fused only in the flame of the oxyhydrogen blowpipe, and in the electric arc. It has a higher specific gravity even than gold, namely, 21.5. It is one of the

few metals that absorb hydrogen, which it does at a red heat. It is not oxidised at any temperature in the air, and is not attacked by any single acid. In these respects it resembles gold, and it is these properties, which render it so extremely useful to the chemist. It is difficult, in fact, to see how the work of the chemist could go on without this metal. Platinum forms brittle alloys with lead, antimony and arsenic, so that compounds of these metals should not be heated in vessels of platinum. Large platinum vessels are used for concentrating sulphuric acid; it is also employed in the construction of electrical apparatus, and thin platinum wire has been used in surgery in special cases.

**356. Antimony** is a silver-white metal with a specific gravity about 6.8, it is hard and very brittle. It melts at  $630^{\circ}\text{C}$ . Antimony is used for the manufacture of tartar emetic (potassium antimony tartrate) and other medical preparations. It is also a constituent of some important alloys such as *type metal*, *Britannia metal* and *plate pewter*; the two last are composed of from 80 to 90 per cent of tin, from seven to 15 per cent of antimony, and small quantities of copper, zinc or bismuth. Type metal contains lead, antimony and tin in the proportions of about two of lead to one each of antimony and tin. The antimony confers upon the alloy the extremely desirable property of expanding on solidification, and it is thus possible to obtain a very accurate cast of the letters.

**357. Bismuth** is a hard, brittle, greyish-white metal, with a reddish tinge. It is used for the manufacture of compounds of bismuth, some of which are employed in medicine and as cosmetics. Bismuth forms alloys with lead and tin, which have a low melting-point (in some cases below  $100^{\circ}\text{C}$ ), and are known collectively as *fusible metal* \*. These alloys possess the remarkable property of expanding on solidification, and are therefore much used in stereotyping.

\* Wood's Metal, which melts at  $60.5^{\circ}\text{C}$ ., is composed of four parts of bismuth, two of lead, and one each of tin and cadmium.

## QUESTIONS.—CHAPTER XXVIII.

1. Write an account of the properties and uses of wrought-iron, cast-iron, and steel.
2. Enumerate the chief alloys of copper, and name the elements that enter into their composition.
3. Compare and contrast the metals lead and copper as regards physical properties. Describe briefly the behaviour of water towards lead.
4. What are "galvanised iron," and "tin plate"? What advantage is gained by coating other metals with zinc and tin?
5. What is the composition of (1) bronze coinage, (2) silver coinage, (3) gold coinage, (4) trinket gold, (5) aluminium bronze? How do these alloys differ from each of the metals of which they are composed?
6. What is the cause of the blackening of silver articles when kept exposed to the air? Which other common metals undergo a change under similar conditions, and which do not?
7. Compare and contrast the metals gold, quicksilver and sodium physically, and as far as you can chemically, *i. e.* as regards their behaviour towards air, water and common acids.
8. What elements enter into the composition of (1) common pewter, (2) type metal, (3) plate pewter, (4) fusible metal, (5) phosphor bronze? Upon what particular properties does the use of these alloys respectively depend?
9. Arrange the common metals in order of (a) their fusibility, (b) malleability, (c) hardness, (d) tenacity, (e) ductility, (f) specific gravity. (N.B.—Note to what extent there is similarity or otherwise in the order in each case.)

## CHAPTER XXIX.

### COMMON METALLIC OXIDES AND HYDROXIDES—LIME, CAUSTIC SODA, etc.

358. **Lime.**—When chalk, or limestone, or any other form of calcium carbonate is heated in the air carbon dioxide is given off, and *quicklime* or calcium oxide ( $\text{CaO}$ ) is left. The change which takes place is represented by the equation



**Manufacture of Lime.**—On the large scale lime is manufactured from chalk or limestone by the process called *lime-burning*, in which the chalk or limestone is heated to bright redness in a kiln which is so constructed that sufficient air can be passed through it to carry away the carbon dioxide as soon as it is set free. The fuel used to heat the chalk may be wood, coke or coal, all of which leave little ash. The materials used should not be too dry, as the steam formed assists in the removal of the carbon dioxide. Two kinds of kilns are still in use. The older form is egg-shaped and has a fire-grate at the bottom. A layer of large pieces of limestone is arranged over this in the form of an arch, and above this smaller pieces are placed until the kiln is filled. A fire is lighted under the arch of limestone, and kept burning for three days and three nights, by which time the whole of the limestone is converted into quicklime and can be raked out at the bottom. This process is intermittent, but is modified in the more modern one so as to be continuous.



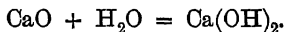
In this process the kilns are bucket-shaped. The fuel and limestone are charged in alternate layers in the proportion of about four parts of limestone to one part of fuel, and at the base of the kiln are gratings and dampers for admitting and regulating the air supply. The lime is raked out at the bottom as the change becomes complete.

Lime prepared in this way contains any impurities present in the original chalk or limestone together with the ash of the fuel used. If required pure, it is made by heating pure marble or calcite or Iceland spar in a platinum dish in a draught of air in a muffle furnace.

**359 Properties.**—Pure lime is a very white and very infusible amorphous substance. When heated to a high temperature it becomes incandescent and gives out a bright white light, the *lime light*. This is used in the optical lantern by heating a cylinder of compressed lime in an oxyhydrogen flame; or in the Welsbach incandescent light by heating a lime gauze in a Bunsen burner. At the temperature of the electric furnace, however, lime can be fused.

**Exp 200** —Take a lump of quicklime, weigh it roughly, and pour on it about one-third of its weight of water. Observe the development of heat, the increase in *bulk*, and the change to a fine dry powder. Weigh afterwards and note increase in weight (after heating in an air oven to drive off excess of water added).

A chemical combination evidently occurs between the lime and the water: the compound *calcium hydroxide* is formed. An equation may be given :



This process is known as *slaking* lime, and the product is called *slaked lime*. The absorption of water with evolution of heat distinguishes *quicklime* (CaO) from slaked lime.

**Exp 201.**—Mix some slaked lime with water. Filter and evaporate some of the solution; note the residue. Test the solution with litmus: it turns blue.

Slaked lime is thus soluble in water, forming *lime water*, it also forms a paste with water, *milk of lime*.

**Exp 202.**—Mix some lime with water in a mortar and pound it into a thick paste. Allow it to stand in the air. It gradually dries, shrinks, and hardens. Test with acid. It fizzes, giving off carbon dioxide.

**Mortars and Cements**—The properties just investigated are made use of in making *mortars* and *cements*. *Mortar* is made by mixing a paste of lime and water with three times its weight of sharp sand. The sand prevents the mass from shrinking and falling to pieces on drying. The causes of the hardening of mortar are (1) loss of water, (2) the conversion of lime into calcium carbonate by the action of atmospheric carbon dioxide, and (3) the chemical combination of the slaked lime and sand to form hydrated calcium silicate, the last cause is, however, the least important.

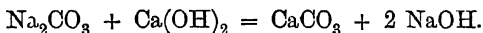
Limestone may contain considerable amounts of impurities. Thus, if the impurity is magnesium carbonate, the lime formed from it will contain magnesia, and will only slake slowly with a small rise of temperature; such lime is called poor. If the impurity is clay (from 15 to 30 per cent), the lime formed will set and harden under water, and is known as hydraulic mortar or *Portland cement*. Portland cement is manufactured on the large scale by burning an intimate artificial mixture of limestone and clay in kilns.

Lime is also used on a large scale in many operations, such as the manufacture of caustic soda, of bleaching powder, and of ammonia, and in the purification of coal-gas, etc. It is also used in agriculture, where its actions on the soil are very varied.

Quicklime absorbs water so readily that it is used for the dehydration of alcohol and for the drying of ammonia, which would combine with the drying agents calcium chloride and sulphuric acid.

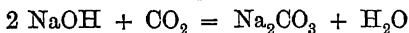
**360. Caustic Soda**, sodium hydroxide,  $\text{NaOH}$ , is manufactured by two processes, (1) the electrolysis of sodium chloride solution, (2) the action of lime on the "red

liquor" obtained in the Leblanc process for the manufacture of sodium carbonate. After the greater part of the sodium carbonate has been crystallised out from the liquid obtained by lixiviating "black ash," a solution remains which contains caustic soda, sodium carbonate, and a number of other substances such as sodium sulphide, sodium cyanide and sodium thiosulphate. This is the "red liquor" already referred to. It is first treated with a current of air which oxidises some of the impurities, *e.g.* the sodium sulphide (which is converted into sodium sulphate), lime is then added and the mixture boiled. A double decomposition takes place between the sodium carbonate and the lime, calcium carbonate being precipitated and caustic soda going into solution.



After settling, the liquid is decanted off and evaporated down in *iron* vessels till all the water is driven off. It is then poured into stick-moulds and allowed to solidify.

Caustic soda is a white deliquescent solid very soluble in water, forming a strongly alkaline solution. Either in the solid state or in solution it rapidly absorbs carbon dioxide from the air, forming sodium carbonate



Caustic soda is used on the large scale in the manufacture of soap and paper and in the refining of oils. *Caustic potash*, potassium hydroxide, KOH, is prepared by boiling potashes (potassium carbonate) with slaked lime. It closely resembles caustic soda in properties, and is used in the manufacture of soft soap.

**361. Spirits of Hartshorn** (*liquor ammoniæ*), ammonium hydroxide,  $\text{NH}_4\text{OH}$ , is manufactured by distilling the ammoniacal gas liquor obtained in the manufacture of coal-gas (see § 285) with slaked lime. It owes its popular name to the fact that it was at one time obtained by the destructive distillation of harts' horns. It is really a very strong solution of ammonia gas in water, and

smells strongly of this gas. Spirits of hartshorn is much used in ice-making machines, *e. g.* that invented by Carré (see § 184), it is also employed in medicine, in the manufacture of colouring matters, and in dyeing and calico-printing. It is a useful laboratory reagent and finds some application for domestic purposes.

**362. Sodium Peroxide**, sodium dioxide,  $\text{Na}_2\text{O}_2$ , is made on the large scale by heating sodium in air which has been freed from carbon dioxide and moisture. It is a white solid when pure, though slightly yellow as usually prepared, and is a strong oxidising agent, on this account it is used in the chemical analysis of refractory minerals such as chrome iron-stone

It reacts with hydrochloric acid, forming hydrogen dioxide, and the liquid so produced is called *soda-bleach*; this liquid is prepared on the large scale and is used for bleaching straw.

**363. Magnesia** (*calcined magnesium* or *magnesia usta*), magnesium oxide,  $\text{MgO}$ , is manufactured by strongly heating *magnesia alba*, a compound of magnesium carbonate and magnesium hydroxide (see § 374), when carbon dioxide and water are driven off and magnesium oxide remains behind as a white powder. Magnesia only combines slowly with water, differing in this respect from quicklime, which, as we have seen, has a great attraction for water, moreover, magnesium hydroxide, the compound produced, is almost insoluble in water, whereas slaked lime is moderately soluble\*. Magnesia is a very infusible substance, and is, therefore, used for making crucibles and fire-bricks. When strongly heated it emits a very bright light, and on this account, pencils of magnesia are employed in the Drummond light. It is also used in medicine.

\* One part by weight of magnesium hydroxide dissolves in 55,000 parts of water, whereas one part of slaked lime requires only 400 parts of water.

364. **Baryta**, barium monoxide,  $\text{BaO}$ , is a white powder chiefly notable for its employment on the large scale in the manufacture of oxygen from the air by Brin's process (see § 75).

**Strontium Hydroxide**,  $\text{Sr}(\text{OH})_2$ , is employed on the large scale in the purification of sugar, and has almost completely replaced barium hydroxide which was formerly used for this purpose, on account of the poisonous nature of the latter substance. It forms a compound with sugar which is insoluble, and can, therefore, be readily purified. On suspending this compound in water and passing in carbon dioxide, strontium carbonate (an insoluble compound) is formed, and sugar goes into solution; the carbonate is removed by filtration and pure sugar crystallised out from the clear liquid.

365. **Red Precipitate**, mercuric oxide,  $\text{HgO}$ , is manufactured by heating mercury and mercuric nitrate together; as thus prepared it is a brick-red crystalline substance. It is very poisonous. When heated it decomposes into mercury and oxygen (see § 12).

366. **Litharge** and **Massicot** are both forms of lead monoxide ( $\text{PbO}$ ). *Massicot* is a yellow solid obtained by heating lead in air to low redness. If a higher temperature is used so that the oxide is produced at a temperature above its melting-point, it forms a red liquid which on cooling solidifies in the form of yellow or reddish flakes, and in this form is called *litharge*. Litharge is used as a glaze for earthenware and in making flint glass. It is also employed in the manufacture of a number of lead compounds such as white lead, red lead, sugar of lead, drying oils and lead plaster. (For behaviour towards water, see under Lead, § 346)

**Red Lead** or **Minium**,  $\text{Pb}_3\text{O}_4$ , is prepared by heating massicot to dull redness for 24 hours in a current of air. It is a red crystalline granular powder, which on heating to a sufficiently high temperature darkens in colour, and

then decomposes into oxygen and litharge. It is largely used in the manufacture of flint glass and paint.

**Puce-coloured Oxide of Lead**, lead peroxide,  $\text{PbO}_2$ , is obtained by the action of nitric acid on red lead

**Exp 203** — Obtain a few grammes of red lead. Place it in a porcelain dish and add dilute nitric acid. Warm gently, and stir with a glass rod till all trace of the original red colour of the red lead has disappeared. The brown powder remaining is the *dioxide*, filter; the filtrate contains lead nitrate, evaporate to smaller bulk and allow this to crystallise out. Wash the residue on the filter with water, and dry it.

Lead dioxide gives off oxygen on heating, leaving litharge. Warmed with strong hydrochloric acid, chlorine is liberated. It is much used in the manufacture of lucifer matches on account of its strong oxidising properties.

**367. Corundum** is the natural crystallised form of alumina or aluminium oxide,  $\text{Al}_2\text{O}_3$ . The pure transparent coloured varieties of corundum are valued as gems, and have received names derived from their colour; thus ruby and sapphire consist of corundum coloured red and blue respectively, the colour being due to the presence of minute traces of impurities. *Emery* is a coarse black impure form of corundum containing oxide of iron; it is used for grinding and polishing metal and glass.

**368. Pyrolusite** is the impure native form of manganese dioxide,  $\text{MnO}_2$ , and is a black solid substance. It is used in the manufacture of chlorine, and in glass making to correct the green tint due to the lower oxide of iron, and so render the glass colourless. It varies much in composition, but usually contains from 55 to 70 per cent. of  $\text{MnO}_2$ ; the chief impurities are ferric oxide, silica and calcium carbonate.

**369. Putty Powder**, stannic oxide,  $\text{SnO}_2$ , is a white powder made by treating tin with nitric acid and igniting the white powder (meta-stannic acid) which is formed, to

drive off water. A poorer quality is prepared by heating tin in air. Putty powder is used for polishing metal, marble, glass and stone, and in making enamels and opaque glass.

\* **Putty**, the substance used by the glazier, is merely a mixture of whiting (levigated chalk) and linseed oil.

**White Arsenic**, arsenious oxide,  $\text{As}_2\text{O}_3$ , is manufactured by roasting (*i.e.* heating in air) native compounds of arsenic. The arsenic is converted into arsenious oxide which volatilises and is condensed in suitable chambers. White arsenic is a white opaque crystalline solid, slightly soluble in water. It is chiefly employed in the manufacture of certain pigments, in dyeing and calico-printing, and in the making of enamels. It is also used in glass making to correct the green colour due to the lower oxide of iron. It is employed in medicine, and as an antiseptic, *e.g.* to prevent "smut" in wheat, and, owing to its very poisonous nature, it is much used as a rat poison. When sold for this purpose it is usually mixed with red lead or powdered charcoal to prevent it being mistaken for other common and harmless substances which have a very similar appearance.

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### QUESTIONS.—CHAPTER XXIX.

1. What is lime? How is it made on the large scale? What is its behaviour towards (a) air, (b) water?
2. What does mortar usually consist of? Why does mortar harden? How could you prove that your explanation was correct?
3. Describe and explain what you observe when you pass carbon dioxide through lime water.
4. How is caustic soda manufactured from "red liquor"? Enumerate the properties of caustic soda. What happens if it is left exposed to the air?

5. What is "spirit of hartshorn"? By what other names is it known? Describe the properties known to you, and mention any of its uses
6. Describe the appearance and chief properties of the following.—Sodium peroxide, magnesia, barytā and red precipitate Give their chemical composition, and mention any purposes for which they are respectively used.
7. What are the chief physical characters and the chemical nature of the following.—Corundum, red lead, litharge and pyrolusite? How can the puce-coloured oxide of lead be got from red lead?
8. What is "white arsenic"? Mention its chief properties. For what purpose is it used?

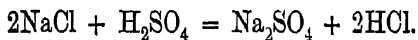


# CHAPTER XXX.

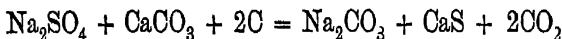
## SECTION I

### COMMON CARBONATES—WASHING SODA, CHALK, etc.

370. **Washing Soda**, or **Soda**, sodium carbonate,  $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$ , is manufactured on a large scale from common salt ( $\text{NaCl}$ ) by two methods. In the first or *Leblanc* process, common salt is converted into *salt-cake* (sodium sulphate) by heating with strong sulphuric acid—

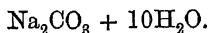


The sodium sulphate is heated with coal and limestone in revolving furnaces, by which the materials are thoroughly mixed. This results in the formation of sodium carbonate—

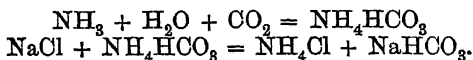


After cooling, the mass is lixiviated, *i.e.* mixed with water, which dissolves out sodium carbonate and a number of other substances in smaller quantity. The calcium sulphide combines with lime and remains behind as an insoluble oxy-sulphide, *alkali waste*, from which the sulphur is recovered by suitable processes. The solution of sodium carbonate is concentrated by heating, and crystals of the composition  $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$  separate out from the hot solution. These are calcined in a reverberatory furnace, when a much purer product (*soda ash*,  $\text{Na}_2\text{CO}_3$ ) is obtained. This is dissolved in water, evapor-

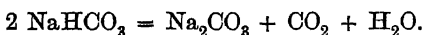
ated, and allowed to cool, and gives large, transparent crystals of washing soda—



The second process is known as the *Solvay* or *ammonia soda* process. It depends on the fact that at ordinary temperatures sodium bicarbonate ( $\text{NaHCO}_3$ ) is less soluble than sodium chloride, ammonium bicarbonate and ammonium chloride. (This illustrates the general rule, that when by the interaction of substances in solution one insoluble substance *can* be formed, that substance *will* be formed.) A strong solution of common salt is saturated with ammonia and well cooled. After cooling, the liquid is run slowly down a cylinder up which a stream of carbon dioxide is passing. A cream collects at the bottom consisting of an aqueous solution of ammonium chloride, etc., with suspended sodium bicarbonate. Equations may be given—



The cream is filtered and the solid sodium bicarbonate heated: carbon dioxide and water are given off, and sodium carbonate is left behind—



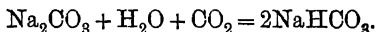
The residue is dissolved in water, and crystallised as washing soda,  $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$ .

**Properties.**—These can be conveniently studied experimentally.

**Exp. 204** —Dissolve some crystals of washing soda in water and note that they are very soluble; concentrate the solution and allow to crystallise. Examine the crystals; they are large and transparent, and possess a glassy lustre. Leave them exposed to the air for some time; they gradually lose water, *i. e. effloresce*, and become covered with an opaque white powder, the composition of which is  $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ .

**Exp. 205** —Test a solution of washing soda with red litmus; the litmus is turned blue, showing that the solution is alkaline. Add a little dilute hydrochloric acid and observe the effervescence produced.

If carbon dioxide is passed through a solution of sodium carbonate, or over moistened crystals of the same salt, sodium bicarbonate is formed—



**Uses**—Sodium carbonate is used in large quantities in the manufacture of glass, soap, and other compounds of sodium. The action of sodium carbonate on greasy materials is very characteristic.

**Exp. 206.**—Take two bottles, and into each put some water and a few drops of olive oil. Into one bottle put some sodium carbonate, and shake them both. The water containing the sodium carbonate becomes creamy and takes very much longer to clear than the other.

Washing soda thus helps to separate oils and fats into small particles, forming *emulsions*, and so enables them to be washed away by water.

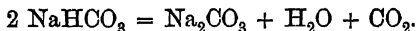
**Exp. 207.**—Pour some sodium carbonate into solutions of calcium sulphate and chloride and magnesium sulphate. Note that precipitates are formed.

Washing soda is thus able to react with water containing lime or magnesium salts and to remove them in the form of a precipitate. This explains its use in removing hardness of water (see § 114).

**Baking Soda**, sodium bicarbonate,  $\text{NaHCO}_3$ , is a white crystalline powder, only moderately soluble in water.

**Exp. 208.**—Show that sodium bicarbonate is much less soluble in water than the normal carbonate, and that the solution is slightly alkaline. Observe the brisk effervescence produced by hydrochloric acid.

On heating sodium bicarbonate it is decomposed with evolution of carbon dioxide and water vapour, leaving a residue of the normal salt.



The same change takes place when an aqueous solution of the salt is boiled. The use of baking soda in cookery depends upon this decomposition, the evolution

of carbon dioxide causing the dough to "rise." Bicarbonate of soda is also used in the preparation of effervescing drinks. For this purpose it is mixed in the dry state with an acid, usually tartaric acid; on adding water the two substances react with the evolution of carbon dioxide which causes the effervescence.

**Exp 209**—Take two test-tubes and half fill them with water. Boil the water in both, then allow them to stand till they have just ceased to boil. Now drop into one a small quantity of bicarbonate of soda; note the effervescence due to the escape of carbon dioxide. To the other add the ordinary carbonate (washing soda). In this case there is no evolution of gas. We may in this way readily distinguish the two carbonates of soda.

**371. Potashes, potassium carbonate,  $K_2CO_3$ .**—The ash of plants contains a notable quantity of potassium salts, chiefly carbonate, and at one time this formed the chief source of potassium compounds. The potassium carbonate was extracted by boiling the ash with water in pots, hence the term "Pot-ashes" (and from this *potash*). Potassium carbonate is now manufactured from potassium sulphate (which occurs in the Stassfurt salt deposits), by a process resembling the Leblanc process for the manufacture of washing soda from sodium sulphate. It is used in the manufacture of glasses which contain potassium, *e.g.* flint glass, and in the preparation of other compounds of potassium.

**372. Sal-volatile** is impure ammonium carbonate. It is manufactured by heating together ammonium sulphate and chalk when double decomposition takes place with formation of ammonium carbonate and calcium sulphate. The ammonium carbonate volatilises and is condensed in cool chambers. Sal-volatile is used to some extent as a baking powder, and it is also employed in dyeing, and in washing woollen fabrics.

**373. Chalk, calcium carbonate,  $CaCO_3$ ,** is usually a white and soft substance and is found in masses which are in many cases some hundreds of feet in thickness.

When examined under the microscope it is seen to be made up of the hard parts of the skeletons of tiny marine animals; their remains must have accumulated in former oceans, and were consolidated by subsequent deposits of a different kind—*e g* clay—until some geological change elevated them above their original position.

When acted upon by dilute acids chalk gives off carbon dioxide and forms a calcium salt of the acid; it often leaves a residue of hard silica or silicates, so that it is for the most part carbonate of calcium which, however, is frequently mixed with silica or calcium silicate.

When well shaken with water the larger particles settle first, and the small particles may be poured off in suspension in the water: they settle later, and are sold under the names of *whiting* and *precipitated chalk*.

Chalk is largely used for polishing, as a colour, as a source of carbon dioxide, and as a source of lime.

**Exp 210.**—Suspend some whiting in water, and pass carbon dioxide through it. Filter the product. Evaporate 10 c.c. of the solution to dryness. Boil some more of the solution to expel carbon dioxide, filter, and evaporate 10 c.c. of the filtered solution. Compare the amounts of residue.

Since in the latter case the residue is much less, we see that chalk is insoluble in pure water, but readily dissolves in water containing carbon dioxide, *i e.* in carbonic acid.

Now the soil water is usually saturated with carbon dioxide, so that in chalk or limestone districts this water becomes saturated with chalk in solution in carbonic acid. These solutions may deposit the chalk on evaporation either as crystalline *calcite* or as stalactites and stalagmites. Examples of the two latter are to be seen in many of the limestone caverns in Derbyshire.

When chalk is heated in the air it loses carbon dioxide and is converted into quicklime, as we have already seen (§ 358), but if it is heated strongly in a confined space so that the carbon dioxide cannot escape, it is

converted into more compact forms of calcium carbonate, namely, *limestone* or *marble*.

**374. Dolomite or Magnesian Limestone** is a naturally occurring substance, consisting of an intimate mixture of calcium carbonate and magnesium carbonate ( $\text{MgCO}_3$ ). It forms very extensive rock masses and is used as a building stone. The Houses of Parliament are constructed of this material. The *mineral* dolomite is a double carbonate of calcium and magnesium, and is not by any means a common substance. Its formula is  $\text{CaCO}_3 + \text{MgCO}_3$ .

**Magnesia Alba Levis** is a basic carbonate of magnesium having the composition  $3 \text{MgCO}_3 + \text{Mg}(\text{OH})_2 + 3 \text{H}_2\text{O}$ . It is produced as a white precipitate when cold solutions of sodium carbonate and magnesium sulphate (Epsom salts) are mixed. It is a very light substance.

**Magnesia Alba Ponderosa** is a much denser basic magnesium carbonate having the composition  $4\text{MgCO}_3 + \text{Mg}(\text{OH})_2 + 4 \text{H}_2\text{O}$ . It is obtained when boiling solutions of sodium carbonate and magnesium sulphate are mixed.

## SECTION II.

### COMMON HALOGEN SALTS.

**375 Sodium Chloride or Common Salt,  $\text{NaCl}$** —This is by far the most important material as a source of sodium salts. In some cases it is obtained in the solid state from mines, but more usually it is brought to the surface in the form of brine and the salt recovered from this by evaporation in pans. On the Continent, in the case of weak brines it is customary to subject the liquor to a preliminary concentration by allowing it to pass over stacks of twigs or brushwood. In England, much of the salt is raised as brine, and some idea may be formed of the extensive use which is made of it, from the fact that

over two million tons of salt are produced annually, three-fourths of this in Cheshire, and the rest chiefly in Worcestershire and Durham. Common salt is used as a glaze for earthenware and for culinary purposes; also as the means of producing "salt-cake" (sodium sulphate), washing soda and "soda ash" (sodium carbonate), and caustic soda, etc.

The properties of common salt should be investigated by a series of experiments such as the following:—

**Exp. 211** —Examine some common salt, and note that it is a white crystalline substance. When large enough, the crystals are seen to be colourless cubes, which have a glassy lustre. Heat a little of the dry salt in a test-tube, and note that the crystals break up with a crackling sound. Next heat a little of the salt on a platinum wire in the Bunsen flame, and note the very bright yellow colour imparted to the flame.

**Exp. 212.**—Place 100 c.c. of water in a beaker, add 50 grammes of common salt, and stir for some time. A portion of the salt will be left undissolved. Filter off the solution and evaporate to dryness: we can determine the exact weight of dissolved salt. It should be about 36 grammes.

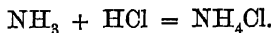
Now heat 50 grammes of salt in 100 c.c. of water to 100°. Filter rapidly while hot, and evaporate the solution. The weight of dissolved salt will be found to be very little more than before. Common salt furnishes an exception to the rule that solids are much more soluble in hot than in cold water.

**Exp. 213** —Take some of the solution of common salt prepared in the last experiment, and test it with red and with blue litmus paper. Since no effect is produced on either, common salt is neutral. To another portion of the solution add a solution of silver nitrate: a white precipitate of silver chloride will be formed.

**376. Potassium Chloride, KCl,** occurs in enormous quantities in the Stassfurt salt deposits, in combination with magnesium chloride as *carnallite*, and this is the chief source of the salt. It very closely resembles common salt in properties, and is chiefly used as an artificial manure and in the manufacture of other potassium salts.

**Potassium Bromide, KBr, and Potassium Iodide, KI,** are very similar to potassium chloride; they are of great importance in medicine and in photography.

377. **Sal ammoniac**, ammonium chloride,  $\text{NH}_4\text{Cl}$ , is manufactured by passing the ammonia produced by heating ammoniacal gas liquor with slaked lime into hydrochloric acid—



The sal-ammoniac is crystallized out from the solution and purified by sublimation. The last process consists in heating the salt in an iron pot provided with a metal cover, the sal-ammoniac vaporises without melting and condenses on the cover in the form of a white tough fibrous mass. It is used in dyeing and in soldering and tinning; it is also employed in medicine and as a reagent in the laboratory.

The liquid in the Leclanché cells, so much used for ringing electric bells, is a solution of sal-ammoniac.

The behaviour of this substance on heating is both interesting and instructive.

**Exp 214** —Place a small quantity of the powdered sal-ammoniac in a *dry* test-tube. Heat gently over the Bunsen flame. Note that the substance (a) passes into vapour *without melting*; (b) settles down higher up the tube as a white deposit (this is an example of a *sublimate*). While still in the flame and therefore fairly hot, lower a reddened litmus paper carefully into the vapours in the test-tube. You will notice that the paper is turned blue in the upper part of the tube but is reddened again a little lower down.

This proves that the sal-ammoniac undergoes decomposition on heating (into ammonia and hydrochloric acid), the lighter ammonia being in excess in the upper part of the tube, the heavier acid gas in the lower.

We can in this way easily distinguish sal-ammoniac from such substances as common salt and potassium chloride, which do not sublime on heating.

**Calcium Chloride**,  $\text{CaCl}_2$ , is obtained as a bye-product in a number of important processes, *e g* in the ammonia-soda process and in the manufacture of potassium chlorate as well as in the preparation of carbon dioxide from marble and hydrochloric acid. Its properties may be investigated as in the following experiment—



**Exp 215** —Examine some calcium chloride. It is a colourless solid, usually in fused masses. Place a few grammes of the solid in a watch-glass on the scale of a balance, and counterpoise. On exposure to the air for half-an-hour, it will be found to have increased in weight. This is due to its absorption of moisture from the air, this property accounts for the use of calcium chloride as a desiccating agent.

Heat a little of the substance on a platinum wire, and note that it gives a red tint to the Bunsen flame. Dissolve a little in water, noting its great solubility; add solution of silver nitrate, and observe the white precipitate.

**Exp. 216** —Shake up in a small flask provided with a sound well-fitting cork, a quantity of benzene with a few drops of water. Notice that the benzene after shaking with the water has a slight milky appearance. Now add some pieces of fused calcium chloride, and shake again. Allow to stand a little while. The benzene will be found to be quite clear again. The water has been removed by the calcium chloride and the benzene is now quite *dry*. It should now be poured off from the liquid (or solid) calcium chloride.

**378. Calomel**, mercurous chloride,  $\text{HgCl}_2$ , is a white crystalline salt insoluble in water. It is prepared by subliming a mixture of mercury and corrosive sublimate ( $\text{HgCl}_2$ ), any of the latter salt which sublimes unchanged being removed by washing with water in which it is soluble. Calomel is also made by adding hydrochloric acid or common salt to a solution of mercurous nitrate; double decomposition takes place and a white precipitate of calomel is formed. This salt is of great importance in medicine.

**Corrosive Sublimate**, mercuric chloride,  $\text{HgCl}_2$ , is manufactured by heating a mixture of mercuric sulphate,  $\text{HgSO}_4$  (prepared by heating mercury with strong sulphuric acid) and common salt, and finally separating the mercury salt by sublimation. Prepared in this manner it is a white crystalline solid readily soluble in water and in alcohol. Corrosive sublimate is extremely poisonous, but in small doses it is a valuable medicine, its solution also possesses powerful antiseptic properties, and is used, for example, in the preservation of insects which are stuffed with cotton wool soaked in mercuric chloride.

**Zinc Chloride**,  $\text{ZnCl}_2$ , is manufactured by dissolving zinc in hydrochloric acid and evaporating off the water. It is a soft white deliquescent solid possessing powerful caustic properties, on account of which it is employed in surgery. Zinc chloride is also used for the purpose of "weighting" cotton.

A solution of zinc chloride is used in soldering, while the fused salt is a useful dehydrating agent (cf.  $\text{CaCl}_2$ ).

**379. Tin Salts** or tin crystals, stannous chloride,  $\text{SnCl}_2 + 2 \text{H}_2\text{O}$ , is made on the large scale by dissolving tin in hydrochloric acid, and allowing the salt to crystallise out. It is used extensively in dyeing and calico printing, and is a useful laboratory reagent.

**Butter of Tin**, oxymuriate of tin, stannic chloride,  $\text{SnCl}_4 + 5 \text{H}_2\text{O}$ , is also employed in dyeing and calico-printing.

### SECTION III.

#### COMMON SULPHATES.

**380. The Vitriols** are well known substances which have been long used for a variety of purposes. They include the sulphates of iron, copper and zinc, known respectively as green, blue and white vitriol. To these, though not usually termed a "vitriol," might be added Epsom salts or sulphate of magnesium, which closely resembles white vitriol in appearance, as well as in some of its properties.

**Green Vitriol, Copperas**, ferrous sulphate,  $\text{FeSO}_4 + 7 \text{H}_2\text{O}$ , is made by dissolving iron in dilute sulphuric acid, and separates out on evaporation in the form of light green transparent crystals. Investigate the properties of the salt as in the following experiment—

**Exp 217.**—Note the beautiful green colour of the crystals. Test their solubility in *cold* water: they require about twice their weight in water for solution. Boil the green solution, and note that it turns brown. This is due to the partial oxidation of the salt from the

ferrous to the ferric state. Heat some of the crystals in a porcelain crucible: a brownish-red residue of ferric oxide is obtained, whilst strongly acid fumes are given off. Fuming sulphuric acid is made (see § 230) by heating this body. To a solution of some crystals in cold water add potassium ferrocyanide: a dark blue precipitate will be produced.

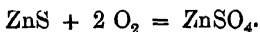
Ferrous sulphate finds important applications in the arts and manufactures; thus it is used in making inks and pigments, *e. g.* Prussian blue, in the manufacture of colcothar and fuming sulphuric acid, and in tanning and dyeing.

381. **Blue Vitriol**, blue stone, cupric sulphate,  $\text{CuSO}_4 + 5 \text{H}_2\text{O}$ , is made on the large scale by roasting *copper pyrites*, a native sulphide of copper and iron; the copper is converted into sulphate and the iron into oxide. On now treating the mass with water, the cupric sulphate dissolves out, leaving the iron oxide as an insoluble residue; the solution is then evaporated and crystallised. Blue vitriol is also manufactured from scrap copper. It is largely used in making pigments, in calico-printing, and in agriculture to prevent smut in seeds. It is also employed in electroplating and electrotyping and in Daniell's electric battery.

The properties of blue vitriol should be studied as follows—

**Exp. 218.**—Observe the fine large blue crystals, which dissolve in four times their weight of water. Heat some of the crystals in a test-tube, and observe that water of crystallisation is given off. Heat to a higher temperature in a porcelain crucible; the remaining water of crystallisation will be driven off, and the anhydrous residue will be found to be almost white. Pour a few drops of water on this white residue. the blue colour is immediately restored.

**White Vitriol**, zinc sulphate,  $\text{Zn SO}_4 + 7 \text{H}_2\text{O}$ , closely resembles Epsom salts in appearance. It is produced when sulphuric acid acts on zinc as in the preparation of hydrogen; white vitriol is manufactured by heating zinc-blende ( $\text{ZnS}$ ) in air when oxygen is absorbed according to the equation—



On lixiviating the mass with water the zinc sulphate dissolves out, and on evaporating the solution and cooling, crystals of the composition  $\text{ZnSO}_4 + 7\text{H}_2\text{O}$  separate. Zinc sulphate is employed for a variety of purposes; thus it is used in the manufacture of drying oils and varnishes, and in dyeing and calico-printing. Also its aqueous solution is much used in pharmacy as a lotion. Zinc sulphate is a poisonous substance.

**Exp 219**—Dissolve some zinc in sulphuric acid, evaporate and allow to cool when colourless crystals of zinc sulphate will separate out. Test the solubility of the crystals in water: they require two- and a-half times their weight of water for solution. Heat some of the crystals in a dry test-tube, and note that they give up part of their water of crystallisation, which condenses in the cool part of the tube.

**382. Epsom Salts**, magnesium sulphate,  $\text{MgSO}_4 + 7\text{H}_2\text{O}$ , is a colourless crystalline substance occurring in sea water and in many mineral waters.

**Exp. 220.**—Examine some crystals of Epsom salts and note that they are colourless prisms. Test the solubility of the crystals in water, they will be found to require about three times their weight of water for solution. Heat some of the crystals in a dry test-tube: the crystals become opaque and lose their water, which condenses in the cool part of the tube.

Epsom salts is prepared on the large scale from the salt deposits at Stassfurt in Germany, which contain considerable quantities of magnesium sulphate associated with other salts. It is used medicinally and also in dyeing.

**383. Calcium Sulphate**,  $\text{CaSO}_4$ , occurs native in a number of different forms. The anhydrous salt is found as *Anhydrite*, *Selenite*, *gypsum* and *alabaster* each contain two molecules of water of crystallisation.

When gypsum is heated to a temperature of about  $140^\circ\text{C}$ , most of its water of crystallisation is driven off and a white mass is left, which when powdered constitutes *Plaster of Paris*. If this powder is made into a paste with water rapid combination takes place with rise of temperature, and in a short time the whole

sets to a hard mass. On this property depends the employment of Plaster of Paris as a cement and for making plaster casts. If gypsum is heated to a temperature of  $200^{\circ}$  C. it loses the property of setting when made into a paste with water; hence care must be taken to regulate the temperature when converting it into Plaster of Paris.

Gypsum is also used as a manure.

*Pearl hardening or annaline* is artificial calcium sulphate, and is prepared by adding dilute sulphuric acid to a solution of calcium chloride, when a white precipitate of calcium sulphate is formed. It is used in paper-making.

Calcium sulphate is slightly soluble in water (one part in 400), and this is one cause of the permanent hardness of water (see § 114).

**384. Salt-cake**, sodium sulphate,  $\text{Na}_2\text{SO}_4$ , is manufactured in enormous quantities by heating common salt with sulphuric acid, and is an intermediate product in the conversion of common salt into sodium carbonate by the Leblanc process (see § 370). On dissolving the anhydrous substance in water and crystallising out, a colourless salt is obtained which contains ten molecules of water of crystallisation. This is called *Glauber's salt*, and is used in medicine as an aperient.

The properties of Glauber's salt should be investigated by performing the following experiment—

**Exp. 221** —Note that it is a crystalline solid, and that when fresh the crystals are transparent and have a glassy lustre. When exposed to the air, they *effloresce*, i. e. give up their water of crystallisation, and become powdery on the surface. Heat some of the salt in a dry test-tube; it fuses, then loses its water, which condenses on the sides of the tube, a white residue of anhydrous sulphate being left. Show that the Bunsen flame is coloured yellow by this salt, as by other salts of sodium.

Salt-cake is used in large quantities in glass-making, in the production of ultramarine, and in dyeing and colouring.

**385. Sulphate of Ammonia**,  $(\text{NH}_4)_2\text{SO}_4$ , is manufactured from ammoniacal gas-liquor by a method similar to that employed in making sal-ammoniac, namely, by heating the gas-liquor with lime and passing the liberated ammonia into sulphuric acid. Ammonium sulphate is very extensively employed as an artificial manure, and it is also used in the manufacture of ammonium alum.

**386 Sulphate of Alumina**, aluminium sulphate,  $\text{Al}_2(\text{SO}_4)_3 + 18\text{H}_2\text{O}$ , is manufactured by the action of sulphuric acid on *china-clay*, which consists of aluminium silicate. It is used as a mordant in dyeing and also for weighting paper.

**Alum**, potash alum,  $\text{K}_2\text{SO}_4 + \text{Al}_2(\text{SO}_4)_3 + 24\text{H}_2\text{O}$ , is manufactured by treating *bauxite*—which is native aluminium oxide containing some ferric oxide—with sulphuric acid, aluminium sulphate is produced, and on adding the requisite quantity of potassium sulphate, evaporating and cooling, crystals of alum separate out.

Investigate the properties of alum as follows:—

**Exp. 222**—Note the large octahedral crystals. Test the solubility of alum in hot and in cold water: its solution requires 18 times its own weight of cold water, but less than its own weight of boiling water. Heat some crystals in a test-tube, and show that water of crystallisation is given off. Show the presence of potassium by the flame test.

Alum is used as a mordant in dyeing and calico-printing, and for weighting paper; it is also employed in medicine.

## SECTION IV.

### SOME OTHER COMMON SALTS.

**387. Saltpetre**, or **Nitre**, potassium nitrate,  $\text{KNO}_3$ , is found in the surface soils in India and Persia where a sufficiency of nitrogenous matter exists, and the climate is sufficiently dry to allow of its accumulation. It is prepared on the large scale by boiling together concentrated solutions of Chili saltpetre ( $\text{NaNO}_3$ ) and

potassium chloride, when a double decomposition takes place and sodium chloride, which at the boiling temperature is the least soluble salt, separates out and is removed by canvas filters; potassium nitrate is crystallised out from the mother liquor. It is also made artificially on the Continent by a method resembling that by which it is formed in the soils of eastern countries. Heaps of ashes are drenched with urine and other nitrogenous refuse, after being exposed to the air for some time the nitrogenous substances become oxidised, and, on lixiviation, the liquor is found to contain large quantities of nitrates. Treatment with potassium carbonate gives rise to the formation of potassium nitrate, which can be extracted in a crude form by crystallisation.

The conversion of the ammonia, produced by the decomposing organic matter, into nitric acid is largely brought about by the agency of *bacteria*. The nitric acid is then converted into nitrate by the potash present in the ashes used.

Saltpetre is a colourless crystalline compound possessing strong oxidising properties, owing to the high percentage of oxygen it contains and the readiness with which it parts with a portion of it to oxidisable bodies. It is for this reason used in making gunpowder (see below); it is also used in medicine and in "salting" meat.

**Exp 223** —Obtain a few grammes of saltpetre, note that it is composed of transparent crystals with a glassy lustre. To about 50 c. c. of boiling water add nitre until no more will dissolve. Pour off the solution from any undissolved crystals, and allow the solution to cool slowly. The nitre will be deposited in beautiful crystals. Heat some of the nitre in a dry test-tube the crystals first crackle, then fuse, and finally, on being strongly heated, give off bubbles of oxygen, a white residue remaining. Observe that this salt gives a violet tinge to the Bunsen flame.

**Gunpowder.**—A mixture of potassium nitrate, charcoal and sulphur finds application as gunpowder, the propelling power of which is due to the fact that the

nitrate supplies oxygen by which the combustion of the sulphur and carbon is effected in a closed space. The volume of the gases generated, even when measured at the standard temperature and pressure, amounts to about 380 times that of the space occupied by the gunpowder, as the temperature generated is over  $2000^{\circ}\text{C}$ , it is evident that the volume is very much greater, and the pressure to which they give rise has been estimated at over 6000 atmospheres, or about 42 tons on the square inch. The composition of gunpowder varies according to the use to which it is to be applied, typically it has the proportions agreeing with the formula  $2\text{KNO}_3 + 3\text{C} + \text{S}$ , and the percentage composition of some forms of it is given in the following table—

	$\text{KNO}_3$	C.	S
$2\text{KNO}_3 + 3\text{C} + \text{S} =$	74.8	13.4	11.8
English military powder =	75.0	15.0	10.0
„ sporting „ =	79.7	12.5	7.8
Ordnance „ =	73.8	13.4	12.8

**388. Chili Saltpetre**, sodium nitrate,  $\text{NaNO}_3$ , is found in the almost rainless districts of Chili, Peru and Bolivia. It is very soluble in water, from which it crystallises as the anhydrous salt in obtuse rhombohedra almost like cubes (hence the name “cubic nitre”). It is largely used as a manure and also in the manufacture of sulphuric acid, nitric acid and potassium nitrate. It cannot be substituted for potassium nitrate in gunpowder owing to its hygroscopic nature.

**Exp. 224** — Obtain some Chili saltpetre. Note that it is very similar to potassium nitrate, but that it gives a yellow coloration to the Bunsen flame. Also show that it absorbs moisture by exposing the powdered salt as in Exp. 215.

**389. Lime Saltpetre or Wall Saltpetre**, calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$ , is a white porous substance often found as



an efflorescence on the walls of stables and other places where liquid manure is abundant. The latter percolates through the walls, and its nitrogen becomes gradually converted into nitric acid by the oxygen of the air assisted by bacteria. As nitric acid is formed it reacts with the lime in the mortar to form calcium nitrate. The solution of this salt finds its way to the outside of the wall where the water evaporates leaving an efflorescence of wall saltpetre.

390. **Silver Nitrate**,  $\text{AgNO}_3$ , is prepared by dissolving silver in nitric acid and evaporating the solution when colourless tabular crystals separate out. By wetting these crystals and pouring the liquid into stick-moulds, *lunar caustic* is obtained. Silver nitrate readily attacks organic matter, thus it is employed for dyeing the hair black, the explanation of the process being that the silver nitrate is reduced to metallic silver, which is deposited as a fine black powder. Silver nitrate also forms the basis of most marking inks; here again the organic matter of the material which is being marked, *e.g.* linen, reduces the silver nitrate and a black deposit of silver is formed.

The properties of silver nitrate should be studied as in the following experiment—

**Exp. 225** —Note the colourless tables in which this salt crystallises. Dissolve some in water, and to one portion add a few drops of hydrochloric acid solution: a white curdy precipitate is formed. Add excess of ammonia solution: the precipitate dissolves, but can again be obtained by adding hydrochloric acid until the solution is acid. Pour the remaining portion of silver nitrate solution on some paper, and expose to sunlight the paper is turned black. Heat a few crystals of silver nitrate in a dry test-tube, and note that the silver nitrate readily fuses.

Silver nitrate is largely employed in medicine; in the form of *lunar caustic* it is applied externally as a cauterant, and although it is poisonous it is also taken internally in small doses. It is also of great importance in photography.

**391. Potassium Chlorate**,  $\text{KClO}_3$ , is manufactured by the double decomposition of solutions of calcium chlorate  $\text{Ca}(\text{ClO}_3)_2$ , (prepared by the action of chlorine on hot milk of lime), and potassium chloride, potassium chlorate being the least soluble salt, separates out first in white crystals. It is a strong oxidising agent, and is used in making matches and fireworks, in the laboratory it is employed as a source of oxygen. Potassium chlorate is also used to some extent in medicine.

**392. Bleaching Powder**, or chloride of lime,  $2 \text{CaOCl}_2 + \text{Ca}(\text{OH})_2$ , is a yellowish-white powder, obtained by allowing chlorine gas to remain in contact with dry and carefully slaked lime for some time. It is manufactured in enormous quantities and used for bleaching, and as a disinfectant.

**Exp 226**—Obtain some bleaching powder; notice that it smells rather strongly of chlorine. Put some in a glass jar and add dilute sulphuric acid, and cover the mouth of the jar with a glass plate. Note that the jar is now full of the green chlorine gas. Test the gas with a moistened litmus paper; the paper will be at once bleached.

**Exp 227**.—Mix some bleaching powder well with water. Dip into this some coloured fabric, now place the piece of cloth in dilute sulphuric acid. Observe that it is soon bleached. The acid liberates chlorine from the powder on the cloth, and this destroys the colour.

Both its bleaching action and its power as a disinfectant are due indirectly to the liberation of chlorine. Even the carbonic acid in the air is sufficient to bring about its decomposition; hence bleaching powder, after exposure to air, always smells of chlorine. To preserve it, therefore, we must exclude the air, that is, keep it in well-stoppered vessels. Wherever chloride of lime is left exposed to the air, all articles of iron or steel whose surfaces are unprotected will be found covered in a short time with "rust." This is due indirectly to the presence of traces of chlorine in the air. This is then an additional reason for keeping bleaching powder in well-stoppered vessels. By mixing chloride of lime with a solution of washing soda, stirring, and then allowing the insoluble

matter to settle, we obtain a clear liquid which serves as a convenient "bleach liquor," and may be used for washing purposes.

**393. Bone Phosphate**, normal calcium orthophosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , is the chief constituent of *bone ash*.

**Exp. 228** — Place some bones on a clear fire. Leave them until they are completely calcined. The organic matter will then have been completely burnt away, and the white residual mass represents the mineral matter of the bones. This is termed *bone ash*. Crush a small quantity to powder and add dilute  $\text{HCl}$ , warm gently; note that the powder almost completely dissolves. You would probably notice also a slight effervescence on adding the acid, since there is always a certain amount of carbonate present in the ash.

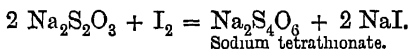
About 80 per cent of bone ash is calcium orthophosphate, but it also contains magnesium phosphate, calcium carbonate and calcium fluoride. Bone ash is used chiefly for the production of artificial manures (see below); it is also employed in certain metallurgical operations, *e g* in the cupellation of silver.

**Apatite** is a naturally-occurring compound of calcium phosphate and calcium fluoride or chloride. Its formula is given as  $3 \text{Ca}_3(\text{PO}_4)_2, \text{CaF}_2$ . It is found in large masses in some parts of the world, as in Spain, and is always present as small crystals in all granitic rocks. The phosphorus of all phosphorus compounds, whether artificial or natural, has been in the first instance derived from the apatite of the igneous rocks.

**Superphosphate of Lime**—This is a mixture of calcium hydrogen phosphate,  $\text{CaH}_4(\text{PO}_4)_3$ , and calcium sulphate,  $\text{CaSO}_4$ , obtained by adding moderately strong sulphuric acid to bone ash, or to any of the natural forms of phosphate of lime. It is soluble in water, and for this reason constitutes a valuable manure. Bone ash itself cannot be used for this purpose as it does not dissolve in water, and hence cannot be taken up by the plant.

**394. Hyposulphate of Soda**, or "hypo," sodium thio-sulphate,  $\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O}$ , is a colourless crystalline substance obtained on the large scale by decomposing

calcium thiosulphate with sodium sulphate. Calcium sulphate is precipitated and is allowed to settle, the supernatant liquid is poured off, evaporated, and allowed to crystallise. It is largely used in photography, on account of the property it possesses of dissolving the haloid salts of silver, also as a mordant in calico-printing, and as an "antichlor" in paper-making. Sodium thiosulphate is also employed to some extent in medicine, and in the laboratory in certain volumetric estimations which depend upon the power of the salt to decolourise iodine, converting it into sodium iodide according to the equation—



**Exp 229**—Take some crystals of sodium thiosulphate. Add them in small portions at a time to a little cold water in a test-tube; observe that they dissolve very readily. Set aside a portion of the solution, and examine it from time to time. You will see that it gradually becomes milky in appearance. This is owing to the fact that it is decomposing. The solid forming in the solution is sulphur. Solutions of "hypo" should therefore be made only when required for immediate use. The crystals themselves are permanent in air and may be kept for an indefinite period.

To a portion of the solution add a little dilute sulphuric acid. Observe that the milkiness appears immediately and is quite pronounced. Add a portion of the solution to a precipitate of silver chloride which has been exposed to light for some time till it is quite dark coloured. Notice what change takes place, if any, and try and find out the reason for it.

**395. Borax**, sodium pyroborate,  $\text{Na}_2\text{B}_4\text{O}_7 + 10 \text{H}_2\text{O}$ , occurs in an impure form as *tinca* on the site of dried-up lakes in India, Thibet and California. The crude native product is purified by recrystallisation from water. Borax is also prepared from boric acid ( $\text{H}_3\text{BO}_3$ ) by treatment with soda ash ( $\text{Na}_2\text{CO}_3$ ).

Borax forms large colourless crystals which are very much more soluble in hot water than in cold. The crystals swell up on heating with loss of water of crystallisation and leave a soft spongy mass of anhydrous borax or *burnt borax*.

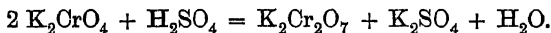
Borax is used in glazing linen and earthenware, to

clean the surfaces of metals preparatory to soldering, and as a flux in the operation of "brazing." It is also employed in the preservation of food, since it possesses antiseptic properties.

**396. Potassium Permanganate,  $\text{KMnO}_4$ ,** is a purple crystalline salt which dissolves in water to produce a dark purple solution, which if very strong may appear almost black. Potassium permanganate readily gives up part of its oxygen to organic matter, and so may be used as a disinfectant. It has recently been found to act as a cure for snake-bite, and great results are anticipated from this discovery.

**Condy's Fluid** is a solution of sodium permanganate,  $\text{NaMnO}_4$ , and sodium manganate ( $\text{Na}_2\text{MnO}_4$ ). It acts like a solution of  $\text{KMnO}_4$ , but is much cheaper, and is largely used as a disinfectant.

**397. Bichromate of Potash,** potassium bichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , is manufactured by heating chrome ironstone with potassium carbonate and lime in the presence of air, extracting the resulting normal potassium chromate,  $\text{K}_2\text{CrO}_4$ , with water, and treating the solution with sulphuric acid when the following change takes place—



The potassium bichromate separates out in large deep orange crystals which have a bitter taste, and are only moderately soluble in water.

Potassium bichromate is a strong oxidising agent, and it is on this account used in the laboratory in the volumetric estimation of iron, and on the large scale in the manufacture of colours from coal-tar, notably alizarin. It is also employed in photography, in dyeing, and calico-printing, in the manufacture of pigments containing chromium, and in the "bichromate" electric cell.

**398. Sugar of Lead,** lead acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3 \text{H}_2\text{O}$ , is a white crystalline solid with a sweetish taste, and is produced by dissolving litharge in acetic acid. It is very

poisonous. *Lead vinegar* is a solution of basic lead acetate obtained by dissolving litharge in sugar of lead. It is used as a lotion for bruises and sores.

399. **Water Glass**, sodium silicate, soluble soda glass is obtained by fusing sodium carbonate and white sand together. It forms a transparent glassy mass, and dissolves readily in water. It has lately come into use for preserving eggs. Eggs placed in a solution of this substance gradually get the surface layer of calcium carbonate of their shells converted into calcium silicate. They are thus rendered quite air tight, and their contents are preserved for some considerable time.

Silicate of soda is also used as a cement in making artificial stone, and for repairing broken porcelain, in soap-making and fresco-painting, and for rendering cloth non-inflammable.

400. **Blende, or Black-jack**, is native zinc sulphide,  $\text{ZnS}$ . It is found associated with galena, quartz and other minerals in the form of crystals, which are sometimes colourless but usually black, owing to the presence of iron. In England the chief localities where blende occurs are Cumberland, Derbyshire and Cornwall. Blende is one of the principal ores of zinc, and is used as a source of the metal and its compounds.

**Galena**, native lead sulphide,  $\text{PbS}$ , is a heavy grey crystalline substance possessing a metallic lustre. It is the most important ore of lead, and frequently occurs in veins in limestone, *e. g.* in Cumberland and Derbyshire.

**Iron Pyrites**,  $\text{FeS}_2$ , is a very widely disseminated mineral occurring in the form of yellow cubic crystals which have a metallic lustre. It is used as a source of sulphur in the manufacture of sulphuric acid. (See § 232.)

## QUESTIONS.—CHAPTER XXX.

## SECTION I.

1. Give an account of one method of preparing washing soda.
2. What is *baking soda*? For what purposes is it used, and how is it affected by heat?
3. By what simple test could you distinguish baking-soda from washing-soda? What is the chemical nature of *potashes*? How did this name originate?
4. How would you show that chalk is changed in properties on being heated in the air?
5. Compare the properties of chalk and quicklime. How would you demonstrate the nature of the change which takes place when chalk is ignited?
6. What is the chemical nature of (1) dolomite; (2) *magnesia alba levis*; (3) *sal-volatile*?

## SECTION II.

1. For what purposes are *common salt*, *potassium chloride* and *potassium iodide* respectively employed?
2. What experiments would you perform in order to investigate the properties of common salt?
3. Give an account of the preparation, properties and uses of *sal-ammoniac*. What happens when it is heated?
4. Write down the chemical names and formulæ of calomel and corrosive sublimate. How would you distinguish between these two substances?

## SECTION III.

1. Give the common names for the sulphates of the metals magnesium, zinc, iron and copper. For what purposes are these salts employed?

2. Describe the experiments you would perform in order to investigate the properties of blue, green and white vitriols.
3. In what natural forms does calcium sulphate occur? How is *Plaster of Paris* made, and on what special property does its value depend?
4. What is *Glauber's salt*, and how is it manufactured? What happens when it is exposed to the air?
5. What is the chemical composition of common alum, and what are its chief uses?

#### SECTION IV.

1. How is saltpetre manufactured? Write down its chemical name and formula.  
What are the constituents of gunpowder?
2. Give an account of the preparation, properties and uses of *lunar caustic*.
3. Write down the chemical names and formulæ of *black-jack*, *galena*, *iron pyrites* and *bone phosphate*.
4. How is bleaching-powder made? Why is it necessary to keep it in well-corked vessels? How would you show its bleaching power?
5. What is bone ash? How could you prepare a sample? What are its principal ingredients? How is it converted into "superphosphate"?
6. For what purposes are the following substances employed—(1) hyposulphite of soda; (2) potassium chlorate; (3) borax?
7. Give the chemical names and formulæ for (1) "hypo"; (2) borax; (3) sugar of lead.
8. How is bichromate of potash manufactured, and what are its chief properties and uses?



## CHAPTER XXXI.

### SECTION I.

#### ROCKS AND SOILS. COMPOSITION OF THE EARTH'S CRUST.

401. **Meaning of the term Crust of the Earth.**—By the term “Crust of the Earth” we understand that portion of the earth's exterior which is accessible to observation. Its thickness is probably not more than about ten or fifteen miles, so that it represents in reality only a relatively thin layer.

Since the average density of the crust, namely 2.8, is just about half that of the globe as a whole, it is clear that the interior must have a very high density and cannot possibly have either the same chemical composition or physical characters as the outer thinner layer.

402. **Rocks.**—Even a cursory examination of any portion of the earth's crust reveals to us that it is composed of masses of material differing in texture and composition. These accumulations we call rocks. A rock may be defined as *any mass of naturally occurring (solid) substance forming part of the earth's crust*. This would necessarily include the loose incoherent sand of the sand-dune as well as the most compact granite.

All the rock masses which go to make up the crust of the earth fall into one or other of two great groups, namely, (a) those which have been formed by the cooling, either at the earth's surface or at some depth below it,

of masses of molten material, and termed *igneous rocks*; and (b) those which have been formed by accumulation of material, derived from pre-existing rocks in a manner to be referred to hereafter; these are termed *stratified, aqueous* or *sedimentary*, and they have been mostly deposited under water. To the former class belong granites and basalts, and the majority of this group are crystalline rocks. To the second belong sandstones, clays, shales and limestones. These are usually of looser texture than the igneous rocks and not, as a rule, crystalline.

403 **Minerals.**—Any given rock on examination usually proves to consist of more than one component, and these can generally be separated, though not always easily, by mechanical means. Such rock components are termed *minerals*, and, whilst a rock may be, and usually is, a substance of not very definite composition, a mineral has a definite chemical composition as well as constant physical characters. We may, in fact, define a mineral as *a naturally occurring substance of definite chemical composition and possessing constant physical properties*. Most minerals, though not all, are crystalline. Those which possess no definite crystalline form are termed *amorphous*. Some are composed of single chemical elements, but the bulk of them are chemical compounds. A list is here given of some of the commoner minerals with their chemical composition, common names and chemical formulæ. It will be seen that many, even the commonest, are bodies of somewhat complex constitution. They are arranged in order of importance as rock constituents.

MINERAL.	CHEMICAL NAME.
Quartz (Rock Crystal).	Silica ( $\text{SiO}_2$ ).
Orthoclase Felspar (Potash Felspar)	Potassium Aluminium Silicate ( $\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 6 \text{SiO}_2$ ).
White Mica (Muscovite).	Potassium Aluminium Silicate.

MINERAL.	CHEMICAL NAME.
Dark Mica (Biotite).	Potassium Iron Magnesium Silicate.
Hornblende.	Calcium Magnesium Silicate, with (usually) Iron Silicate.
Augite	Ditto.
Olivine.	Magnesium Silicate ( $Mg_2SiO_4$ )
Calcite.	Calcium Carbonate ( $CaCO_3$ ).
Gypsum.	Hydrated Calcium Sulphate ( $CaSO_4, 2H_2O$ )
Kaolin.	Hydrated Aluminium Silicate ( $Al_2O_3, 2SiO_2, H_2O$ )
Magnetite.	Magnetic Iron Oxide ( $Fe_3O_4$ )
Iron Pyrites.	Iron Sulphide ( $FeS_2$ )
Hæmatite.	Hydrated Iron Oxide ( $Fe_2O_3, xH_2O$ ).
Diamond.	Crystallised Carbon.
Graphite.	" "
Sulphur (native)	" "

All the above are crystalline minerals.

404. **Elements of the Earth's Crust**—It will be seen that comparatively few elements enter into the composition of the common rock-forming minerals, and, in fact, of the 70 or 80 elements now known to the chemist, about 9 of them constitute 98 per cent. of the earth's crust. These with the approximate proportions of each are given below—

Oxygen	. 50 per cent.	Magnesium	. 2.5 per cent
Silicon	. 25 "	Sodium	. 2 "
Aluminium	. 7.5 "	Potassium	. 2 "
Iron	. 5 "	Hydrogen	. 0.5 "
Calcium	. 3.5 "		
			<hr/> 98.0 <hr/>

There are other elements which, though present in rela-

tively small quantity, are widely diffused and of considerable importance, especially in their relation to life on the earth. These are carbon, nitrogen, phosphorus, sulphur and chlorine. Only six of the above-mentioned elements occur in the free state, viz. carbon, oxygen, nitrogen, sulphur, hydrogen and iron, the last two only in very small quantity.

**405. Weathering of Rocks and Formation of Soils.**—Even the most compact rock on long exposure to the air undergoes a process of disintegration, or “weathering,” as it is termed. This is brought about by such agencies as rain, frost, carbonic acid, and frequent changes of temperature during comparatively short intervals. The effect produced by each agent of weathering will naturally depend on the nature and composition of the rock affected as well as on the climate of the place where the rock is situated. In dry tropical countries temperature changes produce greater effect than they do in this country, where the most important weathering agents are frost, rain and carbonic acid. It will be instructive to examine in some detail the process by which a mass of granite and one of sandstone are respectively disintegrated by this process of weathering.

**406. Weathering of Granite, and formation of Clays, Shales and Sandstone.**—Ordinary granite is composed mainly of the three minerals, quartz, felspar and mica. The felspar alone of these is easily attacked by the carbonic acid of the atmosphere, which is carried to it through the medium of rain water, and, it may be, of dew also. The potash is thus removed as carbonate, being carried away in solution; whilst the silicate of alumina remains as an insoluble powder. Grains of felspar thus become dislocated, with the final result that the whole surface layer of the granite is disintegrated and removed by rain. A fresh surface is then attacked, and so the process goes on, till often a very considerable amount of the once compact granite rock is denuded

away. The materials finally find their way into some river and are carried away and deposited on the sea-floor. The coarser quartz grains with usually a little mica settle down first and give rise to sandstone, further out we have smaller grains with some felspar and mica producing shales, and, further out again, clays, varying in texture and composition, and consisting of the very finest of the disintegrated rock material.

**407. Formation of Clay.**—In clays formed in this way from normally weathered granite there is probably very little kaolin, *kaolin*, of which china-clay is a more or less pure form, is supposed to have been formed in quite a different way. The process has been termed “kaolinisation,” and the action has apparently proceeded from below upwards and not from above downwards. By this process considerable masses of granite come to have their felspar greatly altered, so that the rock mass on exposure afterwards to the weather is soon disintegrated, and the finer kaolin carried away and deposited in lakes, or it may be in the sea. The further from the original granite it is carried the more impure is it likely to become. A great deal, however, of the china-clay employed in the making of pottery is obtained directly from these half-decomposed granite masses, and this is, of course, the purest material.

Other clays again, such as the boulder clays of the northern and eastern counties, have quite a different origin, and may not at all closely resemble in composition either of the two kinds just described, though all are alike in being plastic when mixed with water. This property appears to depend chiefly on the degree of fineness of the particles composing the clay, and not altogether on the particular minerals present. It is important to remember, then, that clay is not by any means a definite substance, but that the term includes a number of materials of varying composition as well as of different origin and different modes of formation.

408. **Weathering of Sandstone.**—An ordinary sandstone consists almost entirely of quartz grains cemented together by means of either ferric oxide, carbonate of lime or silica. Should this cementing material be dissolved away by any means, the grains fall asunder and are washed away by the rain. Now this solution is easily brought about again by the carbonic acid of the air. These quartz grains are carried away by rivers just as those of the granite were, and go to build up the sandstones of a future geological age.

409 **Formation of Soils. Soils formed in situ.**—If the products of weathering remain where they are formed, we have an accumulation of loose material which we call a *soil*. Such a soil would be formed *in situ*. It is clear that this requires special conditions. These are a fairly horizontal surface of the ground and the growth of vegetation. The latter not only prevents the disintegrated material from being as completely removed by rain as it would otherwise be, but it assists materially by its growth the further breaking up of the rock. Plants also increase the normal supply of carbonic acid, since they exhale  $\text{CO}_2$ , and in addition their roots excrete an acid liquid which is quite as effective in the disintegration of the rock as carbonic acid itself. It is easy to see that once a soil has commenced to grow it may continue to increase in thickness, and may reach to quite a considerable depth. Even a compact rock like a granite or basalt may give rise in the same way to soils formed *in situ*, but, as a rule, they will not in such cases attain to any considerable thickness. It is clear that the composition of a soil formed *in situ*, as well as its depth and texture, will vary according to the nature of the underlying rock. These are all factors of importance from the agriculturalist's point of view.

410. **Transported Soils.**—Many soils are practically ready formed as soon as they begin to form part of the dry land. Such are the alluvial deposits laid down in the flatter parts of a river's course, and those that

fill up lake basins. These are termed *transported* soils, and are often of complex nature. To this class belong loams and marls, and in some cases peat.

Soils formed *in situ* are either chalky, sandy or clayey, according as the underlying rock was limestone, sandstone, or clay. These constitute the three chief types of soils, but there are, of course, gradations from the one to the other, especially in the case of transported soils. Marl is a calcareous-clayey soil, and loam is a sand-clay mixture. Sandy soils are "light" to work, that is, are ploughed easily. Clays are heavy, whilst chalky soils are intermediate in character between the two.

All soils contain a certain proportion of organic matter, the product of decayed vegetation. This plays an important part in the composition of soils from the point of view of the agriculturalist. It is known as *humus*.

## SECTION II.

### GLASS—EARTHENWARE—PORCELAIN.

411 Though the number of transparent minerals is large, very few of them occur in crystals or blocks large enough to be used for windows. In fact, if we except quartz, which is hard to work, only mica is left.

The desirability, too, of having vessels which are not porous for the transport and preservation of liquids was soon felt, and among the earliest manufactures we find three, viz. *earthenware*, *porcelain* and *glass*, which were designed to supply these wants.

The common basis of all these is silica,  $\text{SiO}_2$ , which can itself, when pure, as in quartz, be melted in the oxyhydrogen flame, and moulded into any shape when hot. Quartz is transparent, and can be heated or cooled suddenly without cracking.

412. **Glass.**—When silica is heated strongly, with enough soda or potash to make silicates, the mixture melts and becomes homogeneous and transparent. Similarly, with

lime or lead oxide a transparent liquid is produced. When, however, these silicates are allowed to cool, they lose most of their transparency and become crystalline and brittle. They are also readily acted on by water.

If, now, the silicate of soda or potash is mixed with that of lime or lead oxide, and the mixture is melted, the mass cools to a hard, transparent *glass*, which is no longer crystalline, is not readily acted on by water, and can be shaped at a red heat. Glass may be defined, then, as *a transparent, non-crystalline solid consisting essentially of a silicate of an alkali metal combined with either calcium or lead silicate.*

The properties of glass vary to a large extent with the bases of the silicates of which it is composed: thus, excess of soda gives a glass which is easily melted and easily worked, e. g. *crown glass*, used for windows, chemical apparatus, etc., excess of lime gives a tough glass, used for bottle making, excess of potash gives a very infusible glass, used for combustion tubing—it is, however, hard to work, excess of lead oxide and potash gives a heavy *flint glass*, used in the making of lenses for telescopes, etc—it is also very bright and sparkling, and is used in making the best table glass and artificial gems, but it does not resist acids and alkalies, and is not used for chemical apparatus.

The materials used to supply silica in glass making are chiefly quartz, flint and white sand, the lime is supplied by calc spar, marble, chalk or limestone; the soda by soda ash or sodium sulphate and charcoal; the potash by potashes; the lead oxide by red lead or litharge (in each case these substances are in order of desirability). The required quantities, mixed with broken glass to help the fusion, are charged into fire-clay pots heated in a furnace to bright redness. The silicates gradually form and are kept melted until all bubbles of air or carbon dioxide have risen and impurities have settled down. The molten glass is then allowed to cool till viscous, and is blown or rolled into sheets.

Since it is not possible to remove impurities which



have once been placed in the pots, the glass generally contains oxide of iron, which colours it green, and alumina.

The composition of a number of different forms of glass as given in the following table will illustrate this.—

	Silica	Potash	Soda	Lime and Magnesia	Lead Oxide	Alumina and Oxide of Iron.
Bottle glass .. .. (ordinary)	65 6	2·7	4·9	20·4	—	6·1
Window glass .. ..	70 7	—	13·3	13·4	—	1 9
Flint glass .. ..	50 2	11 2	—	—	38·1	0 5
Fusible glass ... .. (for chemical apparatus)	70 5	2 1	17·2	8·7	—	1 0
Infusible glass .. .. (for combustion tubes)	73·1	11·5	3·1	10 7	—	0·9

If the molten glass is allowed to cool quickly, it is hard and brittle; but if cooled slowly, i. e. *annealed*, it retains its toughness.

The colours of glass are due to the presence of certain metallic oxides. Oxide of iron gives it a green colour, as in bottle glass, oxide of manganese gives it a pink or black colour, and is sometimes added to correct the green tint given by oxide of iron; oxide of cobalt gives a blue colour, oxide of chromium, or cupric oxide, green, cuprous oxide, or gold, ruby red. The addition of oxides of tin or antimony as well as bone ash gives rise to the opaque enamel appearance in glass.

**413. Earthenware and Porcelain.**—We have seen in a foregoing section that clay, which forms the basis of all earthenware and porcelain, is derived from a variety of rocks and may vary considerably in composition.

The purest clay, formed from felspars by the washing away of their alkalis, soda and potash, is white and is known as *kaolin* or china-clay; it is represented by the formula  $\text{H}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$ . If it is derived from rocks containing iron, it is coloured yellow or red; or, if the iron has been reduced by organic matter, it is coloured green or blue.

When worked with water the particles of clay stick together and form a tough plastic mass which may readily be moulded into any required shape or turned on a lathe or potter's wheel. When the clay is dried it hardens and the hardness is increased by baking; the resulting product is porous and is known as *biscuit*. To make it impervious and so convert it into *earthenware* it is glazed either (1) by the action of common salt which at the temperature of the kiln is converted into vapour and reacts with the surface layer of the biscuit, forming a thin layer of fusible silicate (sodium aluminium silicate) on the surface of the ware, *salt glaze*; or (2) by coating the ware with a thin layer of a substance which resembles the biscuit in composition, except that lead oxide or some other material has been added to it which renders it more fusible and also transparent. The glaze is ground to a fine powder and suspended in water, the article to be glazed is dipped into the liquid and is then dried and heated strongly, when the glaze melts and forms an even layer over the surface. The product constitutes ordinary table ware.

*Porcelain* is made by incorporating felspar with china-clay and heating the mixture in a furnace to a high temperature, when the felspar melts and fills up the pores of the clay; a certain amount of chemical action takes place and a homogeneous translucent mass results. Owing to the partial fusion which the mixture undergoes, the product must be annealed by slow cooling. It is now glazed by dipping into water containing powdered felspar and flint, and re-heating. Porcelain differs from earthenware in that no part of it is porous, whereas earthenware is porous right through with the exception of the glaze.

414. Bricks may be divided into two classes: (1) those used for building purposes, and (2) those used for furnace linings and called *fire-bricks*. The bricks used for the former purpose are made from common red, brown or blue clays which, as we have seen, may differ much in

composition; but fire-bricks, which have to withstand a high temperature, must be made from infusible material. Now it is found that clay is in general the more infusible the larger the ratio of alumina and silica to alkalis and other basic substances; consequently fire-bricks are made from clay which is composed almost entirely of alumina and silica. Such a clay, which is termed "fire-clay," is found underlying beds of coal in coal-mines. It no doubt represents an ancient soil, and has lost its alkalis to the vegetation which grew upon it in that remote period.

The following table gives the composition of four typical clays:—

	Alumina	Silica.	Ferric Oxide	Lime and Magnesia	Alkalies	Water
Kaolin (Cornwall)	38.6	46.4	—	3.5	1.8	9.1
Stourbridge fire-clay	23.3	63.3	1.8	0.7	—	10.3
Common clay, used for brick making	34.3	49.4	7.7	3.4	—	5.1
Clay for porcelain	36.8	46.8	1.0	2.6	0.3	12.4

The temperature employed in the firing of bricks of pottery varies from a bright red heat in the case of bricks and tiles to a bluish-white heat, somewhat above the melting-point of grey cast-iron, for porcelain.

### SECTION III:

#### PIGMENTS.

**415. Nature of Paint.**—A substance which is used as a paint consists essentially of an insoluble coloured powder or *pigment*, mixed with a liquid or "medium," which dries up when spread out in a thin layer and exposed to the air. The pigment gives the paint its colour and also its *covering power*, i. e. the power it possesses of concealing a surface on which it is spread.

The medium enables the pigment to be conveniently applied to a surface, and on drying binds it firmly to the surface, also in some cases it increases the covering power of the pigment by chemically combining with it.

**416. Characteristics of a good Pigment.**—There are three properties which should be possessed to a high degree by a perfect pigment. They are: (1) *Covering power* or “*body*.” This depends upon the opacity of the pigment; the more opaque a pigment is, the thinner the coat of paint required to conceal the surface to which it is applied. As already mentioned, the covering power of certain pigments is increased by their undergoing chemical combination with the medium with which they are mixed. This is the case with white lead, for example (see § 442). (2) *Permanence*. Pigments differ greatly as regards their power of resisting the various natural agencies to which they may be exposed, such as light, moisture and the gases of the atmosphere. Though in most cases the change which the pigment undergoes is injurious, this is not necessarily so; for instance, air often contains a small quantity of sulphuretted hydrogen, which attacks both white lead and zinc white; in the former case the colour is destroyed because the lead sulphide which is formed is black; in the latter case white zinc sulphide results, so the colour does not change. (3) *Drying action*. Some pigments assist the drying of the medium with which they are mixed by inducing it to absorb oxygen from the air more readily and so become resinified sooner; their action is of a *catalytic* nature (see § 74). Examples of good drying agents, or “*driers*,” are white lead and red lead.

**417 Media.**—In water-colours the medium is of course water; it dries by evaporation. For oil paints a *drying oil* (see § 434), usually boiled linseed oil, is employed; this absorbs oxygen from the air and is converted into a resinous substance. Generally some turpentine is added to thin the mixture down to the required consistency; the greater part of this evaporates

on exposure to the air, but some absorbs oxygen and is resinified (turpentine being also a drying oil).

**418. Oil Paints.**—Owing to the great covering power it possesses, white lead forms the basis of all oil paints except those used by artists, small quantities of other pigments, technically called “stainers,” being added to give the necessary colour. The pigments, after being ground to a very fine powder, are mixed with boiled linseed oil, and the requisite quantity of turpentine is then added.

Brief accounts of a few of the chief pigments will now be given:—

**419. White Pigments.**—**White Lead**, basic lead carbonate,  $2\text{PbCO}_3 + \text{Pb(OH)}_2$ , is the most important white pigment owing to its great covering power, to which reference has already been made. Several processes are used in its manufacture, but the one which gives the most valuable product is the *Dutch process*. In this, lead is converted into basic lead acetate by the combined action of vinegar and air. The basic acetate is then converted into white lead by the action of carbon dioxide.

The disadvantages of white lead as a pigment are that it is not permanent, being blackened by sulphuretted hydrogen, and that it is very poisonous. White lead is very frequently adulterated with barium sulphate or chalk.

**Zinc White**, zinc oxide,  $\text{ZnO}$ , though very inferior to white lead in covering power, has the advantages of being permanent and non-poisonous, and it is largely used as a substitute for white lead, especially in France. It is manufactured by burning zinc vapour in air in large chambers.

**Chinese White** is made from zinc oxide and is much used in water-colouring.

**Permanent White**, barium sulphate,  $\text{BaSO}_4$ , is used to some extent as a substitute for white lead, and, as already mentioned, is often present in white lead as an adulteration. It is permanent and non-poisonous, but

has much less covering power than white lead. Barium sulphate is used for weighting paper.

**420. Yellow Pigments.**—**Cadmium Yellow**, cadmium sulphide,  $\text{CdS}$ , is prepared by precipitating a cadmium salt with sulphuretted hydrogen, and is a permanent pigment.

**Lemon Yellow**, or **Yellow Ultramarine**, barium chromate,  $\text{BaCrO}_4$ , is obtained as an insoluble precipitate by adding potassium chromate to a solution of a barium salt. It is quite permanent.

**Chrome Yellow**, lead chromate,  $\text{PbCrO}_4$ , is made by precipitating a solution of lead acetate with potassium bichromate. It has the disadvantage of all lead pigments, *i. e.* it is blackened by sulphuretted hydrogen.

**Yellow Ochre** is an impure native form of ferric oxide,  $\text{Fe}_2\text{O}_3$ . It is a permanent pigment.

**421. Red Pigments.**—**Vermilion**, mercuric sulphide,  $\text{HgS}$ , is manufactured by heating mercury and sulphur together and subliming the product. The best qualities are, however, made by a wet process. Vermilion is a bright scarlet pigment possessing great covering power, it is quite permanent. It is also used in making red printer's ink.

**Chrome Red**, basic lead chromate,  $\text{PbCrO}_4 + \text{PbO}$ , is obtained by digesting chrome yellow with caustic soda. It is not permanent, being attacked by sulphuretted hydrogen, but it is a good drying agent.

**Colcothar** is the residue which remains on strongly heating green vitriol (ferrous sulphate), and consists of ferric oxide,  $\text{Fe}_2\text{O}_3$ . In addition to its use as a red pigment it is employed as a polishing powder for steel and brass.

**Red Ochre** is an impure native form of ferric oxide.

**Red Lead**, or **Minium**,  $\text{Pb}_3\text{O}_4$ , is prepared by heating massicot ( $\text{PbO}$ ) to dull redness for about twenty-four hours. It is a crystalline powder which, besides being employed as a pigment, is largely used in making flint glass.

**422. Green, Blue and Black Pigments** — **Oxide of Chromium**, chromic oxide,  $\text{Cr}_2\text{O}_3$ , is obtained as a dull green powder by igniting either chromium hydroxide or a mixture of potassium dichromate and sal-ammoniac, and as a bright green powder by igniting mercurous chromate ( $\text{Hg}_2\text{CrO}_4$ ). It is a permanent pigment, and is also used for colouring glass and porcelain.

**Verdigris**, basic copper acetate,  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{Cu}(\text{OH})_2$ , is a blue salt obtained by the action of vinegar (i. e. weak acetic acid) on copper in the presence of air. On treating with water it is converted into green verdigris, another basic acetate. Both these compounds are used as pigments.

**Ultramarine** is a blue pigment prepared by powdering *lapis lazuli*, a blue mineral consisting of a double silicate of sodium and aluminium, together with a compound of sulphur, the exact nature of which is unknown. Ultramarine is also made artificially by heating clay, sand, sulphur and charcoal together, and grinding up the product when cold. It is a very permanent pigment and a good drier.

**Prussian Blue** is made by adding a ferrous salt to potassium ferrocyanide when ferrous potassium ferrocyanide,  $\text{Fe}''\text{K}_2[\text{Fe}''(\text{CN})_6]$ , is precipitated. This is then exposed to the action of the air or other oxidising agents such as chlorine water, when Prussian blue, which consists chiefly of ferric ferrocyanide,  $\text{Fe}'''_4[\text{Fe}''(\text{CN})_6]_3$ , is formed. Prussian blue is not quite permanent; it is however a good drier.

**Ivory Black** is made by heating ivory in retorts out of contact with air. It is a permanent pigment.

**Lampblack** (see § 271) is also used as a black pigment.

## QUESTIONS.—CHAPTER XXXI.

## SECTION I.

1. Define the terms *mineral* and *rock*, and give two examples of each.
2. Give a list of the nine elements of which the earth's crust is mainly composed. Also mention five other elements which are present in smaller quantity but are of great importance.
3. What are the chief agents which bring about the weathering of rocks, and how do they act? Describe in some detail the weathering of granite.
4. What is *soil*? Compare the properties of the three chief types of soils. What is *humus*?

## SECTION II.

1. What is glass, and how is it manufactured? How are its properties affected by (1) rapid cooling, (2) annealing, (3) presence of tin oxide?
2. Describe the process by which earthenware is made from clay.
3. Compare the properties of earthenware and porcelain. How is porcelain manufactured?
4. How are bricks made? Into what two classes may they be divided? In what respects do the two varieties differ?

## SECTION III.

1. Discuss the characteristics of a good pigment.
2. How is paint made? What is the function of (1) the pigment, (2) the medium, in a paint?
3. How is *white lead* made? On what does its special value as a pigment depend? With what substances is it commonly adulterated?



4. Discuss the relative advantages of *white lead* and *zinc white* as pigments.
5. Give the common name, the scientific name and the chemical formula for a yellow, a red, a blue, a green and a white pigment.
6. State briefly how the following pigments are made:  
*vermilion, chrome yellow, red lead, Prussian blue.*

## CHAPTER XXXII.

### SECTION I.

#### THE NATURE OF VEGETABLE AND ANIMAL SUBSTANCES. DETECTION OF CARBON, HYDROGEN AND NITROGEN IN ORGANIC COMPOUNDS.

##### 423. The Composition of Vegetable and Animal Matter.

—Vegetable and animal organisms are built up of a number of chemical compounds, most of which are of a very complex nature. The chief elements which enter into their composition are *carbon*, *hydrogen*, *oxygen*, *nitrogen* and *sulphur*. Very little is known about the constitution of the majority of these compounds, but, during the waste of tissue, many of them break down into simpler substances, and the constitution of a great many of these has been worked out.

It was at one time supposed that compounds produced by life processes could not be prepared in the laboratory; hence the name "*Organic Chemistry*" was given to the branch of Chemistry which dealt with these substances. This view was shown to be erroneous by the German chemist, Wohler, who in the year 1828 succeeded in building up urea ( $\text{CO}(\text{NH}_2)_2$ ) in the laboratory from inorganic material. Since that time innumerable organic compounds have been prepared artificially, and Organic Chemistry is now merely the "Chemistry of the Compounds of Carbon," which are sufficiently numerous to justify their treatment as a separate class.

424. A general idea of the nature and composition of vegetable and animal substances may be obtained from the following simple experiments:—

**Exp. 230.**—Heat in a clean, dry test-tube a small piece of wood. Observe the production of a liquid which is mostly *water* and of combustible gases. Pass the issuing gases into lime water and so prove the presence of *carbon dioxide* in them. Note the black residue which may be completely burnt away on heating again with nitric, thus showing it to be carbon (charcoal). In this way we learn that wood contains, at any rate, carbon, hydrogen and oxygen.

Repeat the experiment using starch, flour, rice or other vegetable product, also with such animal substances as feathers, horn, bone, flesh. Note in the case of animal substances the peculiar and characteristic odour, and also that a gas comes off which turns reddened litmus paper blue—this is ammonia. As before, we have water and a black carbonaceous residue. The ammonia which is evolved is unmistakable proof of the presence in these bodies of *nitrogen*.

A more satisfactory method of proving the presence in organic substances of the elements carbon, hydrogen and nitrogen, as well as sulphur and phosphorus, even when they are present only in relatively small proportion, is described below.

**425. Tests for Carbon, Hydrogen and Nitrogen in Organic Compounds.**—The methods described in the two succeeding experiments may be used for any organic substance (with a few exceptions which we need not consider here).

**Exp. 231.**—Take some powdered pure copper oxide, heat it to redness in a crucible, and allow it to cool in a desiccator; mix with it a little sugar and heat the mixture in a hard-glass tube: note that water (tested by anhydrous copper sulphate, which it turns blue) is formed from sugar and the dry oxide, a proof of the presence of *hydrogen*. Lower a drop of lime water into the tube on a glass rod: it is turned milky; hence carbon dioxide is present, which must have come from *carbon* in the sugar.

**Exp. 232.**—Take a small hard-glass tube, about 0.5 c.m. diameter and 10 c.m. long, which has been closed at one end. Cut a bit of potassium about the size of a pea into three or four thin slices, and introduce it into the tube together with a rather smaller quantity of gelatine: the gelatine should also be cut into three or four small pieces, and these dropped into the tube alternately with the slices of

potassium. Heat the mixture first gently and finally *to redness*. While the tube is still hot, dip it into a small quantity of water contained in an evaporating basin. Care must be taken in performing this last operation, otherwise an accident may occur; hold the tube with a pair of crucible tongs and stand as far away from the basin as you can while dropping the tube into the water. The water in the basin dissolves the potassium cyanide produced by the combination of the potassium with the carbon and nitrogen in the gelatine. Filter, and add to the filtrate ferrous sulphate, ferric chloride, and finally hydrochloric acid. The formation of a blue colour, *Prussian blue*, shows that *nitrogen* was contained in the gelatine.

When the substance burns readily, as, for example, spirit, turpentine, paraffin, and camphor, the presence of carbon and hydrogen may be shown by the formation of carbon dioxide and water.

**Exp 233.**—Put a few drops of spirit on a glass plate, light it, and cover with a dry bell-jar: note the condensation of drops, which may be tested as above (Exp. 231) for water. Invert the bell-jar and plate, pour in some lime water, and shake: note the milkiness, showing the presence of carbon dioxide, and therefore of carbon.

*Sulphur* may be tested for in the filtrate obtained in Exp. 232 by adding to it a few drops of a solution of sodium nitroprusside, when a beautiful purple coloration is obtained if sulphur is present.

*Phosphorus* may be detected by converting it into phosphoric acid by heating the substance gently in a closed crucible with nitre and potassium carbonate. The phosphate formed is then dissolved in nitric acid and ammonium molybdate added, when a yellow precipitate is thrown down.

## SECTION II.

### CARBOHYDRATES—SUGAR, STARCH, etc.

The compounds treated in this section are all closely related and are called *carbohydrates* because they all consist of carbon combined with hydrogen and oxygen, the two latter elements being present in the proportion required to form water. It must be clearly understood,

however, that they are *not compounds of carbon with water*. The sugars will first be dealt with, then starch, dextrin and cellulose.

**426. Sugar.**—The roots, stems and fruits of many plants contain sweet-tasting juices. If their sap is squeezed out and evaporated, or if the roots, etc., are cut into slices and digested with water, which is then evaporated, colourless crystals of sugar are deposited. The chief natural sources of sugar are (1) the sugar-cane and the sugar-beet, which yield *cane sugar*; (2) ripe fruits, *e. g.* grapes, which yield *grape sugar* and *fruit sugar*; (3) milk, from the whey of which *milk sugar* is deposited.

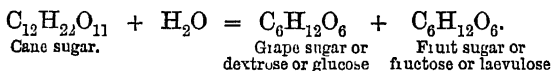
**Exp. 234** —Examine specimens of cane, grape, fruit and milk sugars (1) Taste them: they are all sweet. (2) Boil with a solution of caustic potash. cane sugar does not colour the solution, but the others turn it brown (3) Add a little Rochelle salt (sodium potassium tartrate), then excess of caustic potash and finally some copper sulphate solution. [The object of the Rochelle salt is to prevent the precipitation of cupric hydroxide by the action of potash on copper sulphate] Boil: cane sugar only precipitates red cuprous oxide on long boiling, but the others give a precipitate at once (4) Add a solution of silver nitrate to which excess of ammonia has been added, and warm: the cane sugar only reduces the silver after long boiling, the others do so very soon.

**Exp. 235.**—Boil some cane sugar with dilute sulphuric acid for ten minutes, and test the resultant solution as in Exp 234; it now gives the same reactions as the other sugars.

These properties of possessing a sweet taste and of turning caustic potash brown and reducing copper sulphate and silver nitrate, either at once or after previous boiling with dilute acids, are characteristic of the sugars.

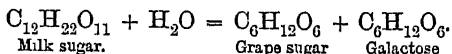
**427. Hydrolysis.**—What is the nature of the change which takes place when cane sugar is boiled with dilute sulphuric acid? It is found that the quantity of sulphuric acid present in the solution after boiling is the same as before. It has not, therefore, undergone any permanent

change.\* One of two alternatives remains, either the water and the sugar have interacted or the sugar alone has suffered some change. The former of these has been shown to be correct, and the reaction, may be represented thus :—



*i. e.* one molecule of cane sugar takes up one molecule of water and then breaks down into a molecule of grape sugar and a molecule of fruit sugar. It is now easy to understand why cane sugar answers to the tests for the other sugars after boiling with a dilute acid.

There are a great number of substances which behave like cane sugar on boiling with a dilute acid, *i. e.* they take up the elements of water and then break down into two simpler substances. This process is termed *hydrolysis*. Milk sugar, which is represented by the same molecular formula as cane sugar,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , yields grape sugar and another sugar called *galactose* (also having the formula  $\text{C}_6\text{H}_{12}\text{O}_6$ ) on hydrolysis with dilute acid.†



**428. Starch.**—An examination of wheat, barley, oats, potatoes, and many other plant stores shows the presence of an opaque white substance which becomes translucent when boiled.

\* With regard to the part played by the sulphuric acid very little is known, and the discussion of the question is quite beyond the scope of this work.

† **Isomerism** —Grape sugar, fruit sugar, and galactose afford an example of a phenomenon very frequently met with amongst compounds of carbon, namely, that of two or more substances possessing the same molecular formula, but different properties. This phenomenon is called *isomerism*, and is explained by assuming that the arrangement of the atoms in the molecules of the respective substances is different. Cane sugar and milk sugar are similarly related.

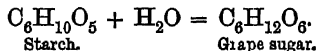
**Exp. 236.**—Take a teaspoonful of flour; put it in a piece of calico about 9 ins square, and bring all the edges together so as to form a bag, dip the bag into a beaker of water, and work the flour between the fingers: the water comes through the calico milky. When the greater part of the flour is worked through into the water allow it to settle. a white powder collects on the bottom. When the water is nearly clear pour it off and dry the residue: it is starch.

**Exp. 237.**—Shake a very little starch in a test-tube of cold water and boil well: the starch partially dissolves, forming a translucent liquid. Allow the liquid to cool and then add a few drops of iodine solution. a blue colour is formed. Boil the blue solution, and the blue colour disappears, to return on cooling.

Starch, then, is a white powder, insoluble in cold water, but partially soluble in hot; it is turned blue by iodine

**Exp. 238**—Boil a little starch with dilute sulphuric acid and test a few drops of the solution from time to time for (1) starch—as in Exp. 237, and (2) sugar—as in Exp. 234. The reactions of starch are gradually lost, and those of sugar appear instead.

This is another example of hydrolysis, the starch being converted into grape sugar. Representing a molecule of starch as  $C_6H_{10}O_5$ —it is really some large multiple of this—the following equation expresses the change which takes place:—



429. The two remaining carbohydrates which will be discussed in this Section, namely, dextrin and cellulose, have the same percentage composition as starch, and are both represented by the empirical formula  $C_6H_{10}O_5$ .

**Dextrin or British Gum** is prepared from starch in the following manner:—

**Exp. 239.**—Place a little dry starch in an evaporating basin in a hot air bath or oven. It gradually turns yellowish, and smells like gum; this product is soluble in water and is used as a gum.

Dextrin is also produced as an intermediate product when starch is hydrolysed by dilute acid. It most probably consists of a mixture of substances with different molecular weights, all having the empirical formula  $C_6H_{10}O_5$ .

**Exp. 240.**—Boil the dextrin prepared in Exp. 239 with dilute sulphuric acid. Test a few drops of the solution after a time (as in Exp 234) and show that sugar is present.

Dextrin on hydrolysis is completely converted into grape sugar.

**430. Cellulose** is the chief constituent of the fibrous parts of plants. Cotton, for example, which consists of fibres attached to the seeds of the cotton plant, and flax which is obtained from the stems of the flax plant, are composed of cellulose together with a small quantity of mineral matter, this may be removed by the action of acids when pure cellulose remains. Wood also consists mainly of cellulose.

Cellulose dissolves slowly in strong sulphuric acid, and on diluting with water and boiling dextrin is formed. On further boiling this is converted into grape sugar. The molecular formula of cellulose is unknown; it may be represented as  $(C_6H_{10}O_5)_n$ .

We shall now briefly consider a few important derivatives of cellulose.

**Collodion and Gun-cotton.**—Cellulose possesses *basic* properties, for, on treating it with nitric acid, it yields nitrates of cellulose and water. The reaction takes place more readily in the presence of strong sulphuric acid which removes the water formed. Cotton wool consists mainly of cellulose, as we saw above, and when this is treated for a short time with a mixture of concentrated nitric and sulphuric acids in the proportion of 1 : 3 a mixture of nitrates called *pyroxylin* is produced. Pyroxylin is soluble in a mixture of alcohol and ether, and the solution is known as *collodion*; it is much used in photography in the preparation of sensitive plates.

If the mixture of acids in the above proportions is allowed to act for 24 hours a larger quantity of nitric acids combines with the cellulose, and an explosive substance called *gun-cotton* is produced, which is much used for blasting; *blasting gelatine* is a mixture of gun-cotton and nitroglycerin.



*Celluloid* is composed of gun-cotton and camphor; it is extensively used for a variety of purposes, *e g.* for making combs and knife-handles. Though not explosive it is very inflammable.

*Cordite* consists of a mixture of gun-cotton, nitro-glycerin and vaseline, it is used as smokeless powder.

431 **Paper** is chiefly composed of cellulose, and was formerly made almost entirely from linen and cotton rags. At the present time, however, the greater part of the paper manufactured is made from esparto grass or wood. Whichever material is used, it is first reduced to small fragments by suitable machinery and then converted into pulp by heating up with caustic soda solution under pressure; in the case of wood, however, a solution of "acid sulphite of lime" (calcium hydrogen sulphite,  $\text{CaH}_2(\text{SO}_3)_2$ ) is used instead of caustic soda as it has been found to be much more effective. The pulp is next bleached by means of bleaching powder, and then sized by the addition of a solution of colophony in sodium carbonate followed by alum, finally substances such as pearl hardening (see § 382) are added to "weight" the paper. The pulp is now run on to an endless belt, the motion of which converts it into a sheet of paper, and when this is sufficiently dry it is submitted to pressure by passing between two rollers.

### SECTION III.

#### OILS AND FATS—SOAP—GLYCERIN.

432. **Nature of Oils and Fats.**—An *oil* may be defined as a liquid which when dropped on glazed paper renders it translucent, and a *fat* as a solid which when melted behaves in a similar manner.

**Exp. 241.**—Allow drops of paraffin oil and olive oil to fall on different parts of a sheet of glazed paper, and note that in both cases the paper is rendered translucent

Oils and melted fats possess other characteristic properties, chiefly physical: thus, they reduce friction between solids, making them feel smooth and greasy; they do not mix with water, but either form a skin over it or form globules in it, when in small quantity. They also burn fairly easily.

Oils and fats are obtained from many sources in the mineral, vegetable and animal kingdoms.

**Mineral Oils**—These have been fully treated in § 288

**Vegetable Oils** are obtained from various parts of plants; some from the stem, e.g. *oil of turpentine*, some from the seeds, e.g. *mustard oil* and *linseed oil*, others from the leaves, e.g. *eucalyptus oil*, and others again from the flowers, e.g. *lavender oil* and *attar of roses*.

We can distinguish two classes of vegetable oils—(1) those which are volatile and are called *ethereal* or *essential* oils; (2) those which are not volatile, and are called *fixed* or *non-volatile* oils.

**Exp 242**—Allow drops of oil of turpentine and olive oil to fall on different parts of a sheet of paper. The oil of turpentine soon disappears, the olive oil does not disappear. The former is a volatile oil, the latter a non-volatile oil.

**433. Ethereal or Essential Oils.**—*Oil of turpentine, eucalyptus oil, mustard oil and attar of roses* are common examples of this class of vegetable oils

Essential oils are usually obtained from plants by one of two methods—(1) The plant-part is extracted with a suitable solvent which dissolves out the oil, the solvent and the oil are then separated by fractional distillation. The chief solvents employed are alcohol, ether and carbon disulphide. (2) The part of the plant containing the oil is first macerated with water and the mixture is then introduced into a still connected with a worm immersed in cold water. The still is heated and a mixture of steam and oil passes over and condenses in the worm from which it runs into a suitable receiver. The oil and water collect in separate layers, the former being usually on the top on account of its lower specific

gravity; sometimes however the oil is heavier than water and then forms the lower layer. The two liquids are separated by decantation.

It is often possible to obtain the oil from a plant-part by distilling it alone instead of with water, but this method is not so satisfactory, for the volatilisation of the oil takes place much more readily in a current of steam. This process of distilling a mixture of substances in a current of steam in order to separate the volatile from the non-volatile constituents is known as *steam distillation*. The method of carrying out a steam dis-

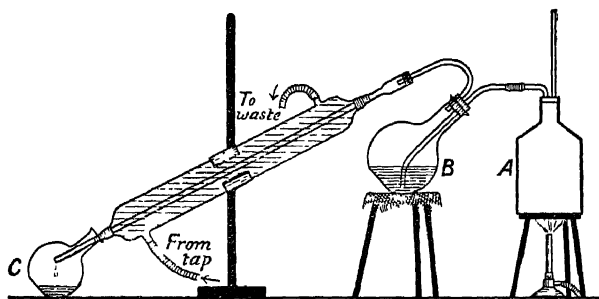


FIG. 79.

tillation as practised in the laboratory will be made clear by an examination of the accompanying figure. Steam is generated in the vessel *A*, and is conducted through the flask *B* which contains the mixture of volatile and non-volatile bodies. A mixture of steam and the volatile substance is carried over through the condenser and collects in the receiver *C*.

In the pure state the essential oils are colourless liquids, but they darken, as a rule, on exposure to the air. They possess characteristic odours which are generally pleasant, and they are the cause of the scent in plants. The essential oils are largely employed in the making of perfumes and essences. Attar of roses

and lavender oil, for example, are employed for the former purpose, and almond oil and oil of peppermint for the latter. Some of them also, such as eucalyptus oil, possess valuable medicinal properties.

The essential oils differ greatly from one another in composition. Some, *e.g.* oil of turpentine, are compounds of carbon and hydrogen only, others, *e.g.* oil of peppermint, contain oxygen in addition, whilst mustard oil contains nitrogen and sulphur but no oxygen.

**Oil of Turpentine** is the most important of the essential oils. It is obtained from *turpentine*, which is the sap of pines and similar trees, and consists of a solution of resins in oil of turpentine. On distilling turpentine in a current of steam oil of turpentine passes over, and the resins remain behind. They constitute the substance called *colophony* which is used as violin resin. Oil of turpentine is a colourless liquid which possesses the useful property of dissolving many substances that are insoluble in water, *e.g.* caoutchouc, resins, sulphur, phosphorus and iodine. Its solvent action on oils and resins is largely utilised in the manufacture of paints and varnishes.

**434. Drying and Non-drying Oils.**—If oil of turpentine is left exposed to the air for some time it dries up, and becomes converted in a resinous substance. For this reason it is called a *drying oil*. Paraffin oil does not behave in this manner, and is an example of a *non-drying oil*. This difference of behaviour on exposure to air is accounted for by the fact that oil of turpentine belongs to the class of “unsaturated” organic compounds, and is thus capable of taking up oxygen from the air and becoming solid. Paraffin oil is a “saturated” compound and cannot add atmospheric oxygen. It therefore remains unchanged.

**435. Non-Volatile or Fixed Oils and Fats**—Some of these are derived from the vegetable kingdom, some from the animal kingdom. Since they possess very similar properties and belong to the same class of

compounds, it will be convenient to consider them together.

The fixed vegetable oils are chiefly derived from the seeds and fruits of plants, and are either extracted by warming and pressure, or by boiling with water and collecting the oil which rises to the surface: among these are *olive oil*, *cotton-seed oil*, *linseed oil* and *colza (rapeseed) oil*.

**Exp 243**—Boil some linseed with water; notice the oil which rises to the surface.

Among the commonest and most important fats and oils derived from the animal kingdom are *butter*, *tallow*, *lard* and *whale oil*. The pure fats are extracted from the tissues containing them by warming and straining or filtering under pressure

**Exp. 244.**—Put some mutton or beef suet into a muslin bag, introduce into a basin of hot water, and squeeze the bag. The fat will melt and run out into the basin leaving the tissue in the bag. On cooling the fat solidifies. It is *tallow*.

Another important fatty product of the animal kingdom is beeswax.

**Butter** is in reality a very complex substance, but it consists essentially of triolein (60 per cent), tripalmitin, tristearin and tributyrin (5 per cent.). It differs from other animal fats in containing such a relatively large proportion of the last-named glyceride. There are in addition water, salts, curds, and colouring matter. The proportion of water may be as high as 15 or 16 per cent. The total fat averages, in unadulterated butter, from 85 to 87 per cent. The rancidity of butter is due to the production of *butyric acid* from the butyrin by a process of decomposition. Like lard, butter contains a large proportion of triolein, and hence is never very hard except in cold weather.

**436. Action of Caustic Potash on Fats and Oils**—The fixed oils and fats behave in a very different manner towards caustic potash from the oils which only contain

carbon and hydrogen, such as the mineral oils and oil of turpentine.

**Exp. 245** —Place some caustic potash solution in four test-tubes and put into them (i.) a small piece of suet or tallow, (ii) some olive or linseed oil, (iii) some oil of turpentine, (iv.) some paraffin oil, respectively; shake up well and allow to stand (i) and (ii) become milky and form a lather; the fat gradually disappears, the oil almost at once, and neither readily reappears, (iii.) and (iv) become milky, but do not form a lather, and the oil soon settles again into a separate layer.

Thus we see that fat and olive oil readily form *soapy* solutions, i. e. are *saponified* by caustic potash; while oil of turpentine and mineral oil are not saponified

In order to find out something about the composition of the saponifiable fats and oils, we must now examine their interaction with potash more carefully.

**Exp. 246.**—Boil some suet with a dilute solution of caustic soda until it is mostly dissolved, pour off the clear liquid, and add to it an excess of hydrochloric acid. there is an immediate white precipitate of flocks of a fatty substance. Collect some of the precipitate on a filter paper, and mix some of it with water. it is insoluble. Add soda solution. the precipitate dissolves, and is again precipitated by the action of an acid. It is probably, therefore, an acid or mixture of acids.

Examination of the flocks prepared in this way from different animal fats shows that they are mixtures, and it is possible to squeeze out by pressure a yellow oil, and leave a white wax-like solid.

The yellow oil consists for the most part of a substance represented by the formula  $C_{17}H_{33}\cdot COOH$ , and called *oleic acid*.

The white solid differs in composition with its source. Thus, from hard fat its composition is represented by  $C_{17}H_{35}\cdot COOH$ , called *stearic acid*, and from softer fats the composition is represented by  $C_{15}H_{31}\cdot COOH$ , called *palmitic acid*.

Oleic acid differs in composition from stearic acid by two hydrogen atoms per molecule; it can hence absorb oxygen from the air, and become resinified or dry

The properties of palmitic and stearic acids are so

similar that they are generally considered together. They are colourless fatty bodies, melting at  $61^{\circ}$  and  $71^{\circ}$  respectively. They are insoluble in water, but soluble in alcohol, benzene, etc., and in solutions of alkalis.

**437. Soaps.**—Palmitic, stearic and oleic acids all combine with bases to form salts, the *soaps*. The alkali salts are produced when fixed fats and oils are treated with caustic alkalis as in Exps. 245, 246, they are soluble in pure water, but insoluble in salt water.

**Exp. 247.—Preparation of Soap**—Boil some suet with caustic soda as in Exp. 246 and to the clear liquid add some salt. Flocks of soap will separate out and rise to the surface. Filter some of them off and boil them with water, they dissolve. Now make a solution of ordinary yellow soap in water and show that when salt is added similar flocks separate, also show that they are soluble in water.

The soaps of the alkaline earth metals, calcium and magnesium, are insoluble in water, and are precipitated by the addition of soap solution to hard water (see §§ 112, 115).

Soap solution has a curious effect on fats and oils, so that finely-divided particles of them do not tend to run together in a soapy solution. Such an intimate mixture of oil particles and water is termed an *emulsion*, and the cleansing properties of soap are due to the formation of an emulsion of any particles of grease by the action of the soapy water (see Exp. 245).

The sodium soaps are harder than the potassium soaps; so that the latter are generally called *soft soaps*. Soap is soluble in alcohol and separates on evaporation as a transparent solid, *transparent soap*.

**Exp. 248**—Cut some shavings of yellow soap and dry them in a water bath till hard, dissolve them in methylated spirit with careful warming and allow to stand. Note the transparency of the product.

*Lead soap*, made by boiling olive oil with lead oxide and water, is used in the manufacture of lead strapping plaster. *Marine soap* is soluble in salt water; it is made from cocoa-nut oil.

**Manufacture of Soap**—Soap is usually manufactured by boiling oils and fats with dilute caustic soda solution till the fat is completely saponified, and then salting out the soap as in Exp. 247. Any impurities in the fat either rise to the top of the soap or else sink. The central portion is boiled up with water and allowed to set. During this boiling various substances are added. Thus, to produce yellow soap a solution of resin in caustic soda is added, and to produce mottled soap sodium silicate and colouring matters are added.

**438. Glycerin.**—If the watery solution which remains after the soap has been removed in the process above described is evaporated down a thick, sweetish liquid is left, which boils at about  $290^{\circ}\text{C}$ . Its molecular composition is represented by the formula  $\text{C}_3\text{H}_5\text{O}_3$ , and it is called *glycerin*. Glycerin is obtained in very large quantities as a bye-product in the manufacture of stearin from fats and oils (see § 443).

As ordinarily seen it is a thick, sweet, colourless liquid, but when quite pure it is a crystalline solid melting at  $17^{\circ}\text{C}$ .; it is very hygroscopic. Glycerin is used in the manufacture of nitroglycerin (see below), stamping inks, flexible glue and toilet soap. It is also employed medicinally and as a food preservative.

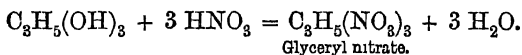
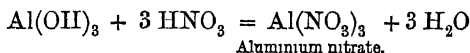
Glycerin does not burn when a light is applied to it unless it has been previously heated to about  $150^{\circ}\text{C}$ .

**Exp 249.**—Apply a light to a little glycerin on a crucible lid. It does not burn. Heat when the temperature has risen sufficiently it will become inflammable.

When glycerin is treated with phosphorus pentachloride it loses three atoms of oxygen and three atoms of hydrogen, and takes up three atoms of chlorine. Now it is found to be a general rule that when phosphorus pentachloride acts on a compound containing hydroxyl ( $-\text{O}-\text{H}$ ) groups, each hydroxyl group is replaced by a chlorine atom. From this it follows that glycerin contains three ( $-\text{O}-\text{H}$ ) groups, and its formula may



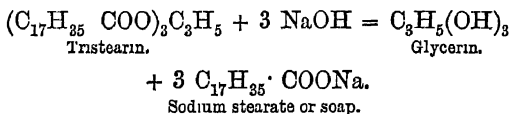
be represented as  $C_3H_5(OH)_3$ , *i.e.* as the hydroxide of a group of atoms  $C_3H_5$ . Further, glycerin behaves towards acids in the same way that hydroxides of the metals do, *i.e.* it forms salts with elimination of water. It is, therefore, a *base*, and the group  $C_3H_5$  acts the part of a metal. To bring this out more clearly let us write the equations for the action of nitric acid on glycerin and on a metallic hydroxide which also contains three ( $-O-H$ ) groups such as aluminium hydroxide,  $Al(OH)_3$ .



Here the group  $C_3H_5$  passes from one compound to another without being broken up just as the atom of aluminium does. It is therefore another example of a *compound radicle*, examples of which have already been discussed in § 183. Also since  $C_3H_5$  acts the part of a *metal*, it is called a *positive radicle*, because on electrolysis a solution of a metallic salt the metal is attracted to the *negative* electrode (see § 325).

**439. Nitroglycerin.**—Glyceryl nitrate is usually called *nitroglycerin*. It is prepared on the large scale by the action of a mixture of nitric and sulphuric acids on glycerin. The function of the sulphuric acid is to take up the water formed according to the equation given above, and so facilitate the reaction. Nitroglycerin is a very explosive substance, and detonates violently when subjected to a slight shock. It is used as an explosive either alone or in the form of *dynamite*, which is a mixture of nitroglycerin and a porous earthy substance called *kieselguhr*. The mixture is less liable to explode suddenly than pure nitroglycerin, and is consequently easier to manipulate. Nitroglycerin is also used in the manufacture of blasting-gelatine and cordite (see § 430).

440. **Composition of Fixed Oils and Fats.**—We have seen that the action of caustic alkalies on the fixed oils and fats is to produce glycerin and the sodium or potassium salts of fatty acids. These reactions become intelligible if we assume that the oils and fats are *salts of glycerin and the corresponding fatty acids*. Thus the fat derived from stearic acid, namely, glyceryl stearate, has the formula  $(C_{17}H_{35} \cdot COO)_3C_3H_5$ , the hydrogen atoms of three molecules of stearic acid being replaced by the trivalent radicle  $C_3H_5$ . This fat is called *tristearin*. The change which takes place when tristearin is decomposed by caustic soda is represented by the equation—



If caustic potash is used instead of caustic soda the reaction is similar, except that potassium stearate (soft soap) is formed instead of sodium stearate.

The formulæ for glyceryl palmitate and glycery oleate are very similar to that of tristearin, being respectively  $(C_{15}H_{31} \cdot COO)_3C_3H_5$ , and  $(C_{17}H_{33} \cdot COO)_3C_3H_5$ ; the former is called *tripalmitin* and the latter *triolein*. The equations for their reactions with caustic alkalies are similar to that given above

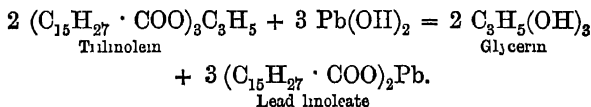
All these three compounds are found in common animal fats—tallow, mutton fat, butter, etc. Tripalmitin derives its name from its occurrence in palm oil, and triolein is so called because it is found in olive oil. Whereas tristearin and tripalmitin are solid at the ordinary temperature, triolein is liquid.

441. **Linseed Oil.**—This oil is extensively employed in making paint on account of its drying properties. It consists largely of the glycerin salt of an acid,  $C_{15}H_{27} \cdot COOH$ , called linoleic acid. On comparing this acid with palmitic acid,  $C_{15}H_{31} \cdot COOH$ , it will be noticed that the former contains the same amount of carbon per

molecule as the latter, but less hydrogen. It is therefore an unsaturated acid, and its glycerin salt, glycerin linoleate, or trilinolein ( $C_{15}H_{27} \cdot COO)_3C_3H_5$ , is also unsaturated, and, like other unsaturated oils, combines directly with the oxygen of the air and becomes ruminified. This explains why linseed oil is a drying oil, whereas olive oil, which only contains a small amount of trilinolein, is a non-drying oil.

It is a remarkable fact that linseed oil dries much more rapidly after heating for some time along with certain substances such as red lead, lead acetate and manganese borate (of which the last is the most effective). The oil which has been treated in this way is called "boiled" oil, and in making paint "boiled" oil is generally employed.

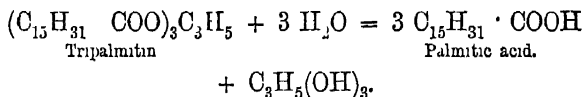
**442. Action of White Lead on Linseed Oil.**—It has already been mentioned in dealing with soaps that litharge (lead oxide) is able to saponify oils. This property is of great importance in the manufacture of paints, for white lead, which is the basis of most paints, consists of a compound of lead carbonate and lead hydroxide, and on mixing this with linseed oil, the lead hydroxide in the white lead reacts with the trilinolein in the oil to produce lead linoleate according to the equation—



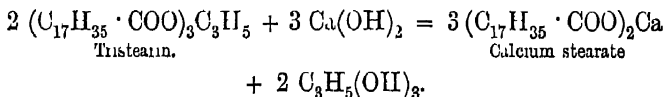
As a result of the formation of this heavy opaque lead salt the covering power of white lead is very great—much greater than that of a compound such as permanent white, which does not react with oils.

**443. Candles.**—Several substances are used for making candles, the chief of which are stearic and palmitic acids, paraffin wax, beeswax, tallow and spermaceti

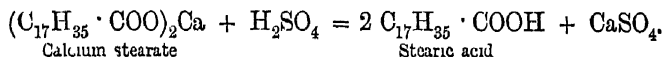
(the wax obtained from the sperm whale) Tallow is very unsatisfactory, as it burns with a nasty-smelling, smoky flame, and gutters badly on account of its low melting-point. The same objections apply to paraffin wax. Most candles are now made from *stearin*, which is a mixture of stearic and palmitic acids obtained on the large scale by the action of superheated steam, lime and water, or dilute sulphuric acid on fats and oils—chiefly tallow and palm oil. If superheated steam or dilute sulphuric acid are used the free acids are liberated. Thus the reaction in the case of tripalmitin is—



If, however, lime is used, a lime soap is formed, *e. g.*—



This is then decomposed by the addition of dilute sulphuric acid, which liberates the free acid.



Whichever method is adopted, a product is obtained which separates into two large layers, the upper consisting of a mixture of stearic, palmitic and oleic acids, and the lower of an aqueous solution of glycerin. The mixture of fatty acids is skimmed off and submitted to pressure to remove the liquid oleic acid. The solid residue constitutes *stearin*, as already stated. *Stearin* candles are composed of *stearin* mixed with a little paraffin wax to render them less brittle.

## SECTION IV.

## FOODS.

**444. Functions of Foods.**—The part which food has to play in the economy of an animal is threefold—(1) it replaces waste tissue, and in a growing animal supplies the new tissue required for this growth; (2) it maintains the temperature of the body at the necessary level ( $98^{\circ}$  F), and (3) it furnishes the energy which the animal requires when it does work.

**445. Nature of Foods.**—A substance which is capable of undergoing oxidation in the body of an animal at the expense of the oxygen which it inhales, may be used as a food for the purposes of (2) and (3); during the oxidation chemical energy is transformed into heat and muscular energy.

The classes of compounds which have been found to fulfil the above condition are *carbohydrates*, *fixed oils and fats* and *albuminoids* or *proteids*. Of these the first two consist, as we have seen, of the elements carbon, hydrogen and oxygen. Albuminoids, however, contain in addition nitrogen and sulphur and sometimes phosphorus. We will consider first the non-nitrogenous compounds. When they undergo oxidation in the body they are converted almost entirely into carbon dioxide, which is exhaled in the breath, and water. Let us consider some of the chief articles used for food. Beginning with those containing carbohydrates, we have bread, potatoes, oatmeal, rice and sago, in all of which large quantities of *starch* are present. Ripe fruits contain *grape sugar* and *fruit sugar*. Again, cane sugar, which is a pure carbohydrate, is a staple article of diet.

Turning to the oils and fats, the most important examples are butter and fat meats

**446. Albuminoids or Proteids.**—On analysing animal tissue it is found to always contain the elements carbon, hydrogen, oxygen and nitrogen. It is clear, therefore, that carbohydrates and oils and fats cannot be used to build up fresh tissue, for they do not contain nitrogen; the only class of bodies which can be employed for this purpose is the albuminoid or proteid class. These are bodies of very complex composition to which as yet no definite formulæ can be assigned; they are all similar in properties to *white of egg* or *albumen*—whence the name *albuminoid*. The term *proteids* is used to imply that these substances constitute the most important part of animal organisms (from the Greek *πρωτεῖον*, pre-eminence). Examples of foods in common use which consist mainly of albuminoids are lean meat, white of egg and milk.

Besides building up tissue, albuminoids are able to fulfil the other functions of a food, for some of the carbon and hydrogen which they contain undergoes oxidation in the body of the animal. An albuminoid, then, constitutes a complete food. It is not, however, advisable to live on a diet composed entirely of albuminoids, for a much larger quantity would have to be eaten to supply the necessary heat and other forms of energy to the body than would suffice to repair wasted tissue. This means that more nitrogen would be taken into the system than could be assimilated, a species of over-feeding. The best diet, therefore, consists of a judicious mixture of nitrogenous and non-nitrogenous foods. In summer time, a smaller quantity of heat-giving foods—bread, potatoes, fat meat, etc.—should be eaten than in winter, because, since the surrounding temperature is higher in summer, a smaller supply of internal heat is required to keep the body at the necessary temperature.

## QUESTIONS.—CHAPTER XXXII.

### SECTION I.

1. What are the chief elements which enter into the composition of organic matter? By whom was an "organic" compound first prepared from inorganic material? In what respect was this discovery of extreme importance?
2. Describe how you would test an organic compound for the elements carbon, hydrogen and nitrogen.

### SECTION II.

1. A solution of cane sugar is divided into two equal parts. One part is boiled for a short time with dilute sulphuric acid, and the following experiments are then performed with each part—(1) the liquid is boiled with caustic potash; (2) Rochelle salt, excess of caustic potash, and copper sulphate solution are successively added to the liquid, which is then boiled, (3) silver nitrate and excess of ammonia are added to the liquid, which is then boiled. State what happens in each case, and explain why the cane sugar behaves differently before and after boiling with sulphuric acid.
2. Explain, with examples, the meaning of the term *hydrolysis*.
3. What do you understand by the term *isomerism*? Give several examples of isomeric bodies.
4. How would you investigate experimentally the change which takes place when starch is boiled with dilute sulphuric acid?
5. Compare the properties of starch and cane sugar. Why are they classified together as carbohydrates?

6. Give two methods by which dextrin can be obtained from starch. What compound is produced when dextrin is boiled with a dilute mineral acid?
7. What is the chemical composition of cellulose? How is pure cellulose prepared, and how may it be transformed into grape sugar?
8. Explain how the following substances are obtained from cellulose, and state for what purposes they are used—(1) gun-cotton, (2) collodion; (3) blasting-gelatine, (4) cordite, (5) celluloid
9. How is *paper* manufactured from wood?

### SECTION III.

1. What is an *oil*? Compare the properties of paraffin and olive oils.
2. Into what two classes can vegetable oils be divided? Give several examples of each class. If you were given a vegetable oil and asked to find out to which class it belonged, how would you proceed?
3. Describe two methods by which essential oils are extracted from plants.
4. Explain the term *steam distillation*, and give an example of the practical use of this process
5. Explain, with examples, the difference between a *drying* and a *non-drying* oil
6. Describe the processes by which (1) fixed oils are extracted from plants; (2) tallow is obtained from mutton suet.
7. The following substances are shaken up well with caustic potash solution and allowed to stand—(1) linseed oil; (2) turpentine; (3) paraffin oil; (4) tallow. State what happens in each case, and explain why these substances do not all behave alike.
8. Explain how you would show that mutton fat is an organic salt. What is a soap?



- 9 How is hard soap manufactured? What is the difference in composition between soft soap and hard soap?
10. What is glycerin? How is it prepared? How would you show that it is a basic body?
11. How is nitroglycerin prepared, and how is it converted into dynamite?
- 12 Explain why white lead possesses so much greater covering power than permanent white
13. What are the chief substances used in making candles, and which substance produces the best candles?
14. What is *stearin*, and how is it manufactured?

## SECTION IV.

- 1 What are the functions of foods in the economy of an animal? Which of these functions are fulfilled by (a) carbohydrates, (b) fixed oils and fats; (c) albuminoids?
- 2 Why is it inadvisable to live on a diet consisting only of albuminoid substances? Explain why less bread, potatoes and fat meat should be eaten in summer than in winter.

## CHAPTER XXXIII.

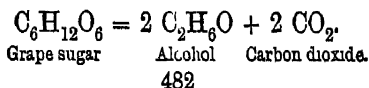
### SECTION I.

#### ALCOHOL, $C_2H_5 \cdot OH$ .

**447. Preparation of Alcohol—Fermentation** —If a solution of grape sugar is left exposed to the air it begins to become turbid and to give off bubbles of carbon dioxide. At the same time *alcohol* or spirit of wine begins to form. The process is termed fermentation, and is brought about in this case by the agency of organisms which are present in the atmosphere. The reaction may easily be investigated.

**Exp. 250.**—Take a large flask and place in it some solution of grape sugar. Place some yeast in the flask and shake it well, put the flask in a warm place and allow it to stand for a few days. Observe the frothing and prove that it is due to the formation of carbon dioxide. After a time, fit the flask with a cork and bent tube connected with a condenser (Fig 80), and distil off a few c.c. of the liquid. Apply a light to a few drops: the liquid burns. Mix a few drops with water, iodine, and caustic potash solution, the characteristic smell of iodoform is noticed.

Thus by the action of yeast on a solution of grape sugar alcohol is formed. Examine the yeast under a microscope and notice that it is composed of small rounded plant-cells belonging to the class of Fungi. This plant, *Saccharomyces (Torula) cerevisiae*, and several others, when immersed in water containing grape sugar convert the greater part of the sugar into alcohol and carbon dioxide according to the equation—



Until recently it was supposed that this change was directly brought about by the living organisms which obtained part of the energy required for building up their cell substance from sugar by splitting it up into carbon dioxide and alcohol. It has now been shown, however, that the liquid which can be squeezed out from the broken plant-cells is just as effective as the living plant-cells, from which it would appear that the active body is a lifeless substance produced during the growth of the plant, and not the plant itself. The term *fermentation* is

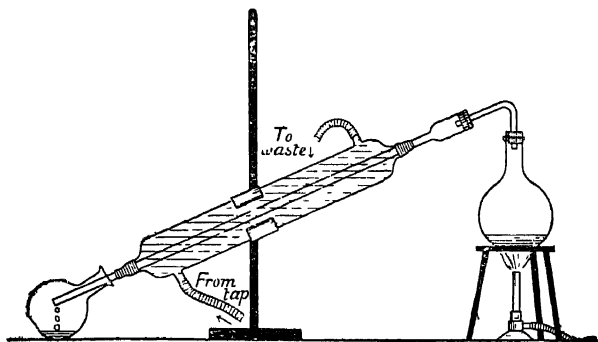


FIG. 80.

applied to the process of the conversion of grape sugar into alcohol and carbon dioxide and to a number of similar processes, and the substance which brings about the change is called a *ferment*, the ferment which decomposes grape sugar is called *zymase*.

Only 95 per cent. of the sugar undergoes the change represented in the equation given above; 3 per cent is changed into glycerin and 0.5 per cent. into succinic acid. Several other compounds are also formed in smaller quantity.

[It may be noted here that, in presence of more oxygen than can be readily dissolved in water, sugar is almost

completely oxidised to carbon dioxide and water, so that in the manufacture of bread only a very small amount of alcohol is formed]

448. Beer and Spirits—When barley is allowed to germinate it gives rise to the formation of a ferment called *diastase*, which is capable of converting starch into a sugar, maltose, isomeric with cane sugar. Maltose, like grape sugar, is readily fermented by yeast with formation of alcohol and carbon dioxide it has been proved, however, that the change takes place in two stages brought about by two different ferments, first the maltose is converted into grape sugar by a ferment *maltase* or *glucase* present in the yeast, and then the grape sugar is changed into alcohol and carbon dioxide by the ferment *zymase*, also present in yeast (as we saw in § 447) On these facts the manufacture of beer and spirits is based In making *beer*, barley which has been steeped in water is spread out in layers and allowed to germinate at a suitable temperature It is then heated up to such a temperature that germination is stopped. The product, which is called *malt*, is next soaked in water and kept for some time at a temperature of  $60^{\circ} - 65^{\circ} \text{C.}$ ; this results in the conversion of the starch into a mixture of dextrin and maltose The liquor (called *wort*) is now run off from the solid matter and boiled with hops, which impart a bitter flavour to the beer and also prevent decay, on account of their antiseptic properties. The wort is cooled to a temperature of  $20^{\circ} - 25^{\circ} \text{C.}$ , and yeast is added when the maltose is converted into alcohol and carbon dioxide, and beer is produced. Since the amount of maltose present is not great, it is usual to add some glucose to the wort; this is fermented by the yeast, and increases the quantity of alcohol in the beer.

*Spirits* are made from barley by a process which closely resembles that used in making beer. The main difference is that the malt is kept soaked in water for a much longer time, till, in fact, *all* the starch has been converted into maltose, instead of only a small part, as

in the case of beer. After the fermentation of the wort the liquid is distilled and the aqueous alcohol which passes over is purified by redistillation, when it constitutes *spirits* (brandy, whisky, etc.).

Wines are made by merely exposing grape juice to the air; the grape sugar present is fermented by yeast, derived from the "bloom" of the fruit.

**Composition of Alcoholic Liquors**—The percentage of alcohol in some of the chief alcoholic liquors is given in the following table—

Brandy	40-50	per cent	Port	20	per cent.
Whisky	40-50	" "	Sherry	16	" "
Rum	40	" "	Claret	7	" "
Gin	35-40	" "	Ale	5 5-6	" "

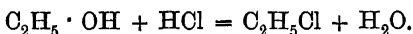
**Purification of Alcohol**—The alcohol prepared by distillation is, as we see from the table given above, mixed with a considerable quantity of water, and is purified by fractional distillation. The final product, *rectified spirit*, has still a little water in it, and is dried by standing over and distillation from quicklime. This removes nearly all the water, and the final traces can be removed, when required, by redistillation with quicklime and collecting only the middle fraction of the distillate.

**449. Properties of Alcohol.**—Pure or *absolute* alcohol is a colourless liquid with a characteristic burning taste and smell. It burns when lighted. It boils at  $78\ 3^{\circ}$  C., freezes at  $-130^{\circ}$ , and has a specific gravity of 79. It mixes in all proportions with water and with ether, and it readily absorbs water vapour from the air. On mixing with water there is a contraction of volume, 52 c.c. of alcohol and 48 c.c. of water making only 96.4 c.c. of the mixture. When mixed with water and poured upon gunpowder and lit, aqueous alcohol will not set fire to the gunpowder if it contains less than 49.3 per cent by weight of spirit. Spirit of this strength is called *proof spirit*.

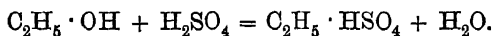
Alcohol is represented by the formula  $C_2H_6O$ , which

is based on its percentage composition and molecular weight only, or by  $C_2H_5 \cdot OH$ , as the hydroxide of a positive radicle  $C_2H_5$  or *ethyl*, i.e. a radicle resembling the radicle  $C_3H_5$  of glycerin (see § 438). The latter formula is supported by the fact that alcohol acts like a base, forming salts (*ethereal salts*) and water by the action of acids

Thus when mixed with hydrochloric acid and heated under pressure a chloride, ethyl chloride,  $C_2H_5Cl$ , is formed—



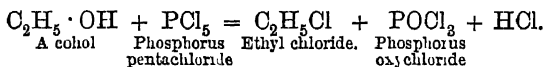
When warmed with concentrated sulphuric acid an acid sulphate is formed, ethyl hydrogen sulphate,  $C_2H_5 \cdot HSO_4$ —



The following facts afford confirmatory evidence of the correctness of the formula just given.

(i.) Sodium dissolves readily in alcohol, replacing one atom of hydrogen and forming a body, sodium alcoholate or *sodium ethylate*, represented by the formula  $C_2H_5 \cdot ONa$ . This shows that one atom of hydrogen in alcohol is different from the other five.

(ii.) Phosphorus pentachloride acts readily on alcohol, removing one oxygen and one hydrogen atom, and putting one chlorine atom in their place, thus forming ordinary ethyl chloride,  $C_2H_5Cl$ . These two atoms must hence be arranged in the molecule in the form of a hydroxyl ( $-O-H$ ) group. One of the hydrogen atoms, then, is directly united to oxygen and differs in this respect from the other five. The equation representing the change which takes place is—

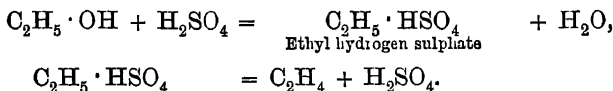


(iii.) None of the hydrogen atoms in ethyl chloride are replaceable by sodium, from which it follows that the hydrogen atom in ethyl alcohol which is replaceable by sodium, is the one contained in the hydroxyl group.

Alcohol dissolves many substances insoluble in water, *e. g.* resins, etc., and so is much used in manufactures. To prevent the drinking of this alcohol, which does not pay duty as a food, it is *methyiated* by adding 10 per cent. of crude wood spirit and as much paraffin as it will dissolve. On the Continent bone oil is often added for the same purpose.

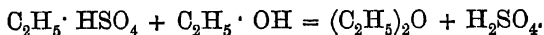
**450 Action of Sulphuric Acid on Alcohol.**—We have seen that alcohol dissolves in concentrated sulphuric acid with the formation of ethyl hydrogen sulphate. This salt undergoes two very interesting decompositions—(1) when heated with excess of the sulphuric acid, (2) when heated with excess of alcohol.

(1) When heated with excess of concentrated sulphuric acid the salt splits into water and *ethylene gas*. The reaction may be represented by the equations—



This reaction has already been used in § 280, for the preparation of ethylene.

(2) When heated with excess of alcohol the salt forms an oxide of ethyl, *ether*, or *ethyl ether*. The reaction may be represented thus—



**Preparation of Ether. Exp. 251.**—Fit up a flask with a condenser, dropping funnel, and thermometer reaching nearly to the bottom of the flask (Fig. 81), in the flask place a mixture of about equal volumes of sulphuric acid and alcohol and heat it on a sand bath or asbestos to about 140°. Fill the dropping tube with a mixture of alcohol and sulphuric acid, and allow it to trickle in from time to time: a volatile liquid comes over with a characteristic smell of ether.

**451. Properties of Ether.**—Ether is a volatile, mobile, colourless liquid of specific gravity  $\cdot 72$ , boiling at  $35^{\circ} \text{C.}$ , and solidifying at  $-129^{\circ}$ . Its percentage composition and molecular weight are represented by the formula  $\text{C}_4\text{H}_{10}\text{O}$ . When rapidly volatilised the heat which is rendered latent in the ether vapour is supplied by any bodies with which it is in contact, and they become very cold, so much so that an ether spray is largely used to produce local cooling.

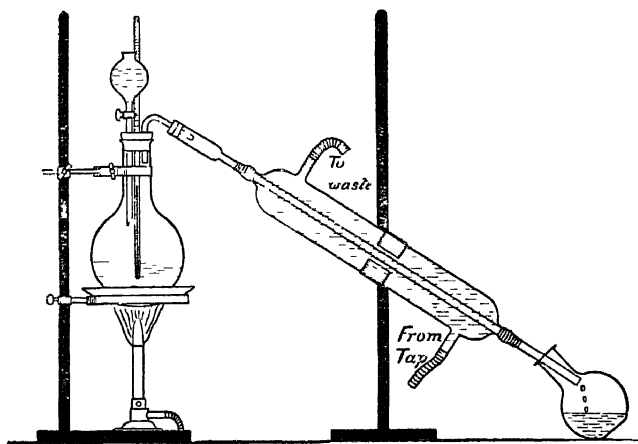


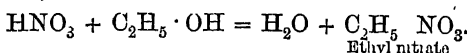
FIG 81.

**Exp 252** —Take a small beaker and place it on a few drops of water on a block of wood; put some ether in the beaker, and blow air through it by means of a tube and bellows the ether cools, the water freezes, and the beaker sticks to the wood.

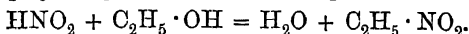
Ether acts as a solvent, and is able to extract many bodies from their solutions in water. It has also a valuable anæsthetic action Ether burns in air, and explodes with oxygen. Care must always be taken to evaporate ether only on a water bath and without a flame very near it,



**452. Action of Nitric Acid on Alcohol.**—We should naturally expect that the action of nitric acid on the base alcohol would be to form the salt ethyl nitrate and water. This reaction does take place to a greater or less extent depending upon the conditions of concentration, temperature, etc



But alcohol is easily oxidised, so that part of the nitric acid is reduced by it to nitrous acid which combines with a further quantity of the alcohol to form *ethyl nitrate*,  $\text{C}_2\text{H}_5 \cdot \text{NO}_2$ , according to the equation—



**453. Action of Oxidising Agents on Alcohol.**—Oxidising agents *e.g.* chromic acid or alkaline permanganate solution, oxidise alcohol very readily to *aldehyde*.

**Exp 253** —Take two or three drops of alcohol in a test-tube and add potassium bichromate solution and sulphuric acid; warm the mixture: the chromic acid turns green from reduction, and a new and characteristic fruity smell is noticed—the smell of aldehyde.

Aldehyde has different properties from alcohol, and its composition and molecular weight are represented by the formula  $\text{C}_2\text{H}_4\text{O}$ . Since its formula differs from that of the parent alcohol,  $\text{C}_2\text{H}_6\text{O}$ , by two hydrogen atoms, it is called *al-de-hyde*, which is a contraction for *alcohol de hydrogenatum*.

Aldehyde is a colourless mobile liquid with a characteristic fruity smell and burning taste. It boils at  $21^\circ \text{C}$ . It is soluble in water and alcohol.

Nitric acid, chromic acid, and other oxidising agents are readily reduced by aldehyde—more readily than by alcohol.

**Exp 254** —Take a solution of silver nitrate in a test-tube; add to it a few drops of ammonia solution until the precipitate which is at first formed redissolves; then add a few drops of potash solution until the solution becomes slightly turbid. Add a few drops of aldehyde: the silver is reduced, more quickly on warming, in the form of a lustrous metallic lining to the tube, the *silver mirror*.

Sodium amalgam reduces aldehyde again to alcohol.

**Exp 255**—Boil a few drops of aldehyde in a test-tube with a strong solution of caustic potash; it turns yellow and then brown from the formation of aldehyde resin

From these reactions we see that aldehyde has similar properties to grape sugar, and we may infer that they belong to the same class of bodies.

## SECTION II.

### COMMON VEGETABLE ACIDS—ACETIC ACID, OXALIC ACID, TARTARIC ACID.

**454. Acetic Acid,  $C_2H_4O_2$ —Preparation.**—We have just prepared aldehyde from alcohol by oxidation, and have noticed that it possesses reducing properties, *i. e.* that it is readily oxidised. It is therefore advisable to examine the products of oxidation of the aldehyde, *i. e.* the products of further oxidation of alcohol. For this purpose the aldehyde, or alcohol, is submitted to the action of the oxidising agent for some time.

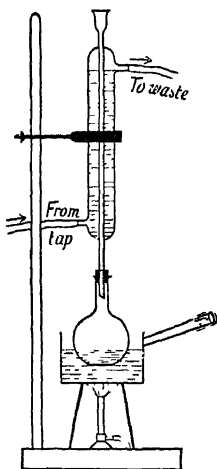


FIG 82.

**Exp. 256.**—Take a half-litre flask, fitted with a cork and upright condenser so as to run the distillate back into the flask (see Fig. 82); place in the flask about 20 gms. of potassium bichromate covered with dilute sulphuric acid (one in five). Warm by a water bath and pour down the condenser a few c.c. of aldehyde or alcohol: the smell gradually changes to that of vinegar. Turn the condenser down by fitting it with a bent tube, and heat the flask, collect the dis-

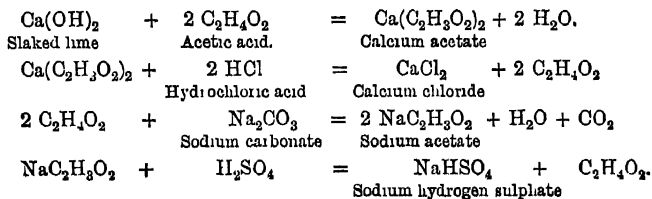
it with a bent tube, and heat the flask, collect the dis-

tillate coming over between  $110^{\circ}$  and  $120^{\circ}$ , test it with litmus, chalk, etc. : it is acid.

The acid, a dilute solution of which has been prepared in the above experiment, is called *acetic acid*; its percentage composition and molecular weight are represented by the formula  $C_2H_4O_2$ .

**455. Manufacture of Acetic Acid.**—Acetic acid is obtained on the large scale from pyroligneous acid, *i. e.* the acid produced by the destructive distillation of wood. The pyroligneous acid, which consists of a mixture of water, acetic acid, methyl alcohol and acetone, is treated with lime, which converts the acetic acid into calcium acetate, and then distilled to remove methyl alcohol and acetone. The residual liquid is evaporated down, and the tarry substances which rise to the surface are skimmed off. The evaporation is finally carried to dryness and the residue of calcium acetate gently ignited to burn away organic matter as far as possible. The purified salt is next distilled with concentrated hydrochloric acid in copper vessels, when a strong solution of acetic acid passes over. The acid is further purified by redistilling with potassium bichromate, and now contains no impurity except water. To remove this the solution is neutralised with sodium carbonate and the sodium acetate ( $NaC_2H_3O_2 \cdot 3H_2O$ ) produced is crystallised out; the crystals are ignited to drive off the water of crystallisation, and the anhydrous salt distilled with concentrated sulphuric acid, when pure anhydrous acetic acid passes over and collects as a colourless liquid.

The equations representing the reactions involved in the above process are as follows—



**Exp 257.**—Take a small retort, place in it about 5 or 10 gms of calcium or sodium acetate, cover it with strong sulphuric acid, heat carefully (Fig 83), and collect the product. it is a pungent-smelling liquid. Test it with litmus.

**456 Vinegar**—When beer or wine turns sour, the alcohol present is converted into acetic acid and *vinegar* is produced. The change is brought about by the action of the vinegar plant, *Bacterium aceti*, a fungus which is present in the air, and which is able to cause the oxygen of the air to oxidise alcohol into acetic acid.

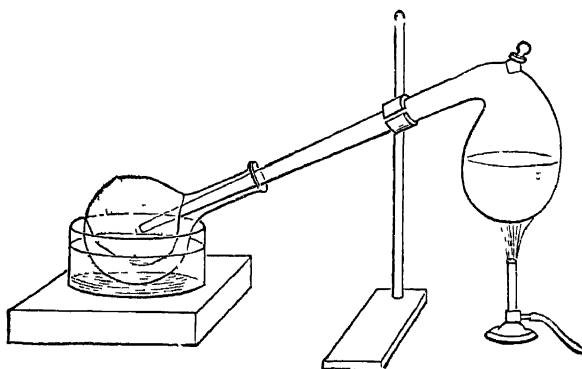


FIG 83.

Vinegar is made on the large scale by allowing dilute spirit—either fermented malt liquor or poor wine—to run slowly over faggots which have been impregnated with vinegar from a previous (similar) operation. The faggots are contained in a large cask between two perforated discs placed respectively a short distance from the top and bottom of the cask. Air is admitted through a ring of holes just above the lower disc, and the unused air (chiefly nitrogen) passes out through an opening in the top of the cask. As the dilute spirit descends through the cask it becomes converted into vinegar under the influence of the active fungus present in the vinegar with which the faggots were impregnated.

**457. Properties of Acetic Acid**—Pure acetic acid is a colourless liquid of specific gravity 1.055. It blisters the skin and has a characteristic pungent smell, which, on dilution, is like that of vinegar. When cooled by immersion in a freezing mixture acetic acid freezes to a colourless crystalline substance, melting at  $16.5^{\circ}\text{C}$ , and called *glacial acetic acid*. Acetic acid boils at  $118^{\circ}\text{C}$ , and the density of its vapour has the peculiarity of being nearly twice as great just above its boiling-point as at higher temperatures, it has been supposed that it has a higher molecular weight at low temperatures than at high ones. Each molecule at the lower temperature may, perhaps, be represented by  $(\text{C}_2\text{H}_4\text{O}_2)_2$ . It acts as a solvent for many bodies which are insoluble in water, e.g. sulphur and phosphorus.

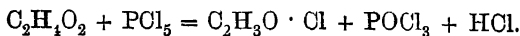
**Exp 258**—Apply a light to some acetic acid in a basin: it does not burn. Heat the basin and apply a light to the boiling acid: its vapour now burns.

Chlorine acts upon acetic acid and substitutes three chlorine for three hydrogen atoms in succession, producing three different compounds, monochloroacetic, dichloroacetic, and trichloroacetic acids, which possess properties very similar to those of acetic acid itself. The formation of these compounds is represented by the following equations—



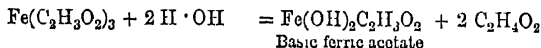
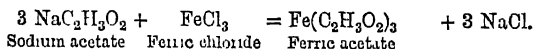
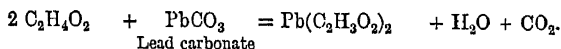
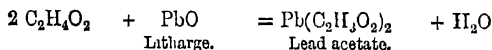
Hydrochloric acid and sulphuric acid have no action on acetic acid, nor have nitric acid, chromic acid or oxidising agents generally, but an alkaline solution of potassium permanganate is able to oxidise it (to oxalic acid). Phosphorus pentachloride acts on acetic acid,

substituting one chlorine atom for hydroxyl, and forming *acetyl chloride*,  $C_2H_3O \cdot Cl$ , a fuming liquid

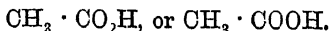


**458. Acetates.**—The most characteristic compounds of acetic acid are its salts, prepared by the direct reaction between the acid and bases or basic oxides. Acetic acid is a monobasic acid, *i. e.* it only contains one atom of replaceable hydrogen per molecule. All its normal salts are soluble in water, but they are frequently decomposed by boiling water and give precipitates of basic salts

**Exp 259**—Neutralise some acetic acid with soda and crystallise out the sodium acetate, dissolve litharge or lead carbonate in moderately strong acetic acid and crystallise out lead acetate (sugar of lead), add a solution of acetate of soda to ferric chloride. a red solution of ferric acetate,  $Fe(C_2H_3O_2)_3$ , is seen. Neutralise and boil this, and a brown precipitate of basic ferric acetate,  $Fe(OH)_2C_2H_3O_2$ , comes down



**459 Constitution of Acetic Acid.**—We have now sufficient data to decide on the formula of acetic acid, and so arrange it thus—



This formula embodies the following facts—

(1.) One atom of hydrogen (that in the  $COOH$  group) is replaceable by metals and one hydroxyl group by chlorine under the action of phosphorus pentachloride.

(2.) Three hydrogen atoms (those in the  $CH_3$  group) are different from the other one, and can be replaced by chlorine without destroying the acid characters of the body.

(iii) Acetic acid is closely related to aldehyde ( $C_2H_4O$ ) and alcohol ( $C_2H_5 \cdot OH$ ), from which it is formed by oxidation

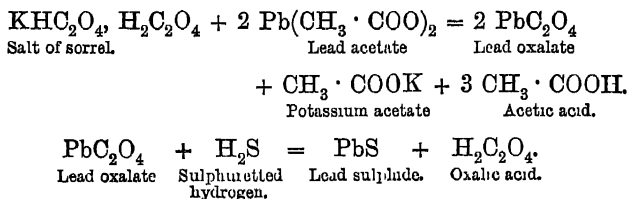
The group of atoms  $CO_2H$  or  $COOH$  is characteristic of organic acids, and is called *carboxyl*.

**460. Oxalic Acid,  $C_2H_2O_4 + 2 H_2O$ —Preparation.**—When sorrel or rhubarb juice is evaporated a crystalline salt is formed, which is decomposed on heating, leaving potassium carbonate behind and forming carbon monoxide and carbon dioxide. This suggests the presence of a salt of potassium with an organic acid; so we must try to prepare the acid by precipitating the potassium salt as a lead salt by the addition of lead acetate, and then precipitating the lead as lead sulphide by sulphuretted hydrogen.

**Exp. 260.**—Dissolve 10 or 15 gms. of salt of sorrel in water, add a solution of lead acetate; filter the precipitate and wash it well; suspend the precipitate in water and pass in sulphuretted hydrogen, when all the lead is precipitated as lead sulphide, filter and evaporate the filtrate: crystals separate out.

The crystals so obtained dissolve in water, producing a solution which turns blue litmus red and forms salts and water by the action of bases, they consist of an acid, *oxalic acid*,  $H_2C_2O_4$ , combined with two molecules of water of crystallisation, and are represented by the formula  $H_2C_2O_4 + 2 H_2O$ .

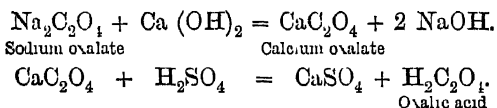
The following equations represent the reactions involved in the preparation of the acid as described above—



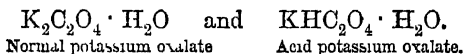
Oxalic acid is also produced by the action of nitric acid on carbohydrates such as sugar and wood fibre

**Exp 261**—Warm some sugar with nitric acid in a small flask, when the action becomes vigorous remove the flame. After a time crystals of oxalic acid separate out, recrystallise them from water.

**461. Manufacture of Oxalic Acid**—Oxalic acid is manufactured by the action of hot caustic soda on sawdust or other forms of woody tissue. The mixture is heated on iron plates when sodium oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ ) is formed. This is dissolved in hot water and converted into insoluble calcium oxalate ( $\text{CaC}_2\text{O}_4$ ) by the action of lime. The calcium salt is filtered off and decomposed by sulphuric acid, when calcium sulphate and oxalic acid are produced. The calcium sulphate is filtered off, and the filtrate evaporated when crystals of oxalic acid separate out.



**462 Properties of Oxalic Acid.**—Oxalic acid is a fairly strong acid possessing very poisonous properties. It dissolves metallic oxides without rapidly acting on the metal, and so is used in cleaning tarnished metallic surfaces. Oxalic acid is a dibasic acid, *i. e.* it forms two series of salts, the normal and the acid, these are represented in the case of the potassium salts by the formula—



**Exp. 262**—Make a strong solution of oxalic acid, measure any volume, say 10 c.c., and add caustic potash solution from a measuring glass or burette till it is neutral to litmus paper. Now add the same volume of caustic potash solution to 20 c.c. of the acid. Evaporate both solutions and crystallise out the salts. Prove that one is acid, the other neutral, and also that they contain different percentages of potash by igniting equal weights of each in crucibles and weighing the residues. Oxalic acid forms two different salts with potash, and is therefore dibasic.



Since it is found that, as a general rule, the basicity of an organic acid depends upon the number of carboxyl groups it contains we may infer that oxalic acid contains two of these groups; the formula of the anhydrous acid may therefore be represented  $\text{COOH} \cdot \text{COOH}$ , and of the hydrated acid,  $\text{COOH} \cdot \text{COOH} + 2 \text{H}_2\text{O}$ .

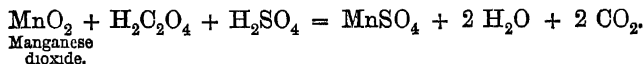
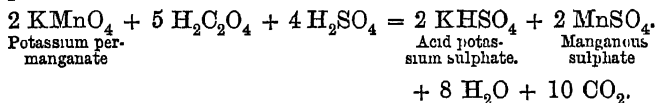
Oxalic acid also forms salts composed of one molecule of the acid oxalate of an alkali metal and one molecule of oxalic acid; such salts are called *quadroxalates*, and of these potassium quadroxalate or salt of sorrel (also called salt of lemon),  $\text{KHC}_2\text{O}_4$ ,  $\text{H}_2\text{C}_2\text{O}_4 + 2 \text{H}_2\text{O}$ , is the best example.

A large number of oxalates are known of which the most useful and characteristic are those of potassium and sodium already referred to, and calcium oxalate,  $\text{CaC}_2\text{O}_4$ , which is insoluble in acetic acid, but soluble in hydrochloric acid.

Chlorine, hydrochloric acid, and nitric acid have no action on oxalic acid, but it is readily oxidised to carbon dioxide and water by potassium permanganate or manganese dioxide and dilute sulphuric acid.

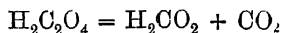
**Exp 263** —Take a solution of oxalic acid, add a little dilute sulphuric acid, and warm it to  $60^\circ$ ; run in a few c c. of potassium permanganate solution: this salt is decolourised, and bubbles of a gas are given off, which is proved to be carbon dioxide by lime water. Repeat the experiment, using manganese dioxide instead of potassium permanganate: the manganese dioxide dissolves, and the oxalic acid is again oxidised to carbon dioxide and water. In each case manganous sulphate should be proved to be in the solution.

The equations representing the reactions which take place are—

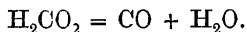


Heat decomposes oxalic acid; the acid first splits off  
 M. CHEM. K K

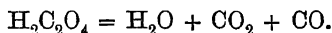
the water of crystallisation and then decomposes further into formic acid ( $\text{H}_2\text{CO}_2$ ) and carbon dioxide



Part of the formic acid breaks up further into carbon monoxide and water.



Some of the anhydrous oxalic acid, however, sublimes unchanged. Hot, strong sulphuric acid breaks oxalic acid up completely into water (absorbed by the sulphuric acid), carbon monoxide and carbon dioxide.



Oxalic acid is used to remove black ink stains and iron-moulds; salts of lemon is also employed for the same purpose.

**463. Tartaric Acid,  $\text{C}_4\text{H}_6\text{O}_6$ —Preparation.**—When the juice of ripe succulent fruits is evaporated crystals generally separate, mixed with sugar. The crystals dissolve in water, and may be purified by recrystallisation in presence of dilute sulphuric acid, or of carbonic acid, or of alcohol, which makes the crystals less soluble. The aqueous solution of these crystals turns blue litmus red and neutralises bases; the crystals, therefore, consist of an acid which is called *tartaric acid*.

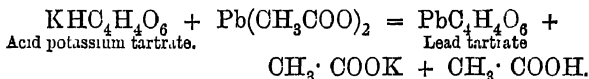
In the natural fermentation of grape juice, carbon dioxide and alcohol are formed, which cause the precipitation of an insoluble crystalline substance called *argol* which yields potassium carbonate on ignition. The argol is recrystallised, and forms *cream of tartar*. When heated it chars and forms potassium carbonate, so it appears probable that the original-tartar is a potassium salt of an organic acid.

To test this perform the following experiment—

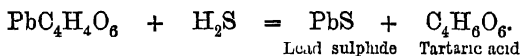
**Exp 264.**—Dissolve some cream of tartar in water, and add lead acetate. Filter off the white precipitate which is produced, suspend

it in water and pass in sulphuretted hydrogen for some time. Filter off the black precipitate of lead sulphide which results, concentrate the filtrate and allow to cool. Crystals will separate out which when dissolved in water turn blue litmus red; they consist of *tartaric acid*.

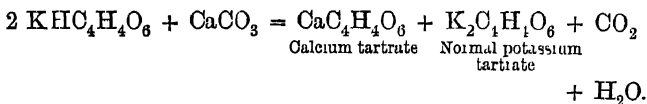
The explanation of the changes brought about in the Experiment just described is as follows—Cream of tartar consists of acid potassium tartrate,  $\text{KHC}_4\text{H}_4\text{O}_6$ ; this on treatment with lead acetate yields a white precipitate of lead tartrate according to the equation—



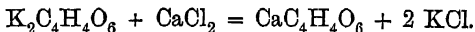
The lead tartrate is decomposed by sulphuretted hydrogen with formation of tartaric acid which dissolves and lead sulphide which is precipitated



**464. Manufacture of Tartaric Acid.**—On the large scale tartaric acid is manufactured from cream of tartar in the following manner.—The cream of tartar is dissolved in water and boiled with chalk, when the following change takes place—

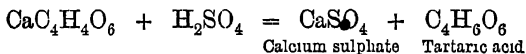


Calcium tartrate, being insoluble, is precipitated while normal potassium tartrate remains in solution. The calcium salt is filtered off and calcium chloride added to the filtrate; this converts potassium tartrate into calcium tartrate which is precipitated, and potassium chloride goes into solution.



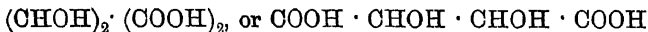
The precipitate is again separated by filtration, and the two precipitates are washed with water to remove soluble

salts. The calcium tartrate is next treated with the calculated quantity of dilute sulphuric acid required for its decomposition according to the equation—



Insoluble calcium sulphate is precipitated and tartaric acid goes into solution. On filtering, evaporating the filtrate, and cooling, crystals of tartaric acid separate out.

**465. Constitution and Properties of Tartaric Acid.**—Tartaric acid forms two series of salts, and two only, with different amounts of caustic potash solution; so that it is probably a dibasic acid, containing two carboxyl groups. It is acted on by hydrobromic acid with the substitution of two bromine atoms for two hydroxyl groups; so that it probably contains two basic hydroxyl groups as well. The best way in which a formula can be arranged to agree with these facts is—



The presence of so many hydroxyl groups is accompanied by instability under the action of heat, sulphuric acid, and oxidising agents, even silver salts being reduced by the acid.

**Exp 265.**—(1.) Heat some crystals of tartaric acid alone and with concentrated sulphuric acid, and notice the decomposition products; they consist of free carbon, carbon monoxide, carbon dioxide and sulphur dioxide

(ii) Shake up a silver solution with ammonia and potash as in Exp 254, and add some cream of tartar solution; warm and observe the silver mirror.

The two tartrates of potassium are of interest, the normal salt,  $2 \text{K}_2\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$ , being soluble, and the acid salt, cream of tartar,  $\text{KHC}_4\text{H}_4\text{O}_6$ , being rather insoluble in water. Rochelle salt, a double tartrate of sodium and potassium,  $\text{KNaC}_4\text{H}_4\text{O}_6 + 4 \text{H}_2\text{O}$ , is also useful on account of its solubility.

As the acid is solid, the formation of tartrates by its means is of interest.

**Exp. 266.**—Mix some crystals of dry tartaric acid with dry sodium carbonate or bicarbonate in a beaker, no action can be seen, and the air in the beaker may be tested for carbon dioxide. Now add a few drops of water a violent fizzing is noticed, and carbon dioxide is given off, test it.

Thus, when substances are not in chemical contact they do not react; water brings about contact. This property is utilised in the manufacture of effervescing salts and baking powder.

The tartrates of the heavy metals are interesting, as they are insoluble in water, but soluble in cream of tartar solution, with formation of soluble double tartrates. These double tartrates are also soluble in excess of alkali; so that they prevent the precipitation of these metals by alkalies.

Use is made of this property in making up an alkaline solution of a copper salt, *Fehling's solution*, and also soluble preparations of iron and of antimony, *tartar emetic*, for example, is obtained by dissolving antimony oxide ( $\text{Sb}_2\text{O}_3$ ) in cream of tartar.

**Exp 267.**—(i.) To a very strong solution of potassium salt add a solution of tartaric acid, and rub the inside of the containing vessel with a glass rod. the insoluble acid salt, hydrogen potassium tartrate (cream of tartar), separates out

(ii.) To a solution of ferric chloride add tartaric acid in excess, and then add excess of ammonia solution. the solution turns brown, but no precipitate of ferric hydroxide is formed.

(iii.) To a solution of copper sulphate add Rochelle salt and then caustic potash in excess. no precipitate appears even on boiling, though the solution turns to the blue colour characteristic of alkaline solutions of copper.

## SECTION III.

### OTHER COMMON ORGANIC SUBSTANCES.

466 **Benzene**,  $\text{C}_6\text{H}_6$ , a most important substance from a chemical point of view, and one also which finds some applications in the arts, is obtained by the fractional

distillation of coal-tar, which contains besides benzene a great number of other benzene derivatives. The first fraction known as "light-oil," and boiling up to  $150^{\circ}$ , contains practically all the benzene. This is subjected to further fractionation, and tolerably pure benzene is obtained. Benzene is a colourless, mobile liquid with a characteristic smell (which reminds one of an escape of gas). It is lighter than water, with which it will not mix. It is highly inflammable and burns with a white, smoky flame. It is a useful solvent for resins, fats, sulphur, phosphorus, india-rubber, etc. It is used for removing grease-stains from clothing. *Benzine*, with which it may be confounded, is quite a different substance. This latter is one of the lower boiling fractions obtained in the distillation of crude petroleum or rock oil. It is used in the preparation of burning oils. It is not by any means a simple substance, but contains many bodies of quite a different class chemically from benzene.

467. **Carbolic Acid**, phenol,  $C_6H_6O$ , is a colourless crystalline substance melting at  $42^{\circ}C$ . It is only sparingly soluble in cold water, but dissolves more readily in hot water. On exposure to the air it gradually turns pink. Carbolic acid possesses powerful antiseptic properties and is much used as a disinfectant. It is a powerful poison. It has a slightly acid reaction. If just neutralised with caustic soda, and ferric chloride added, a violet coloration is produced. This together with its characteristic smell would serve as a means of distinguishing it from other common substances.

468. **Hydroquinone**,  $C_6H_6O_2$ , is a colourless crystalline substance soluble in water. It is used as a developer in photography. On warming with ferric chloride it is converted into its oxidation product quinone, which forms yellow crystals on the sides of the test-tube and which may be recognised also by their characteristic odour.

**469. Pyrogallie Acid,\*** pyrogallol,  $C_6H_6O_3$ , is similar in appearance and properties to hydroquinone, and is also used as a photographic developer. Its solution in caustic soda readily absorbs oxygen from the air and turns brown. It is therefore used for the estimation of oxygen in gas analysis. It gives a red colour with solution of ferric chloride.

**470. Tannin, Tannic Acid,** is a colourless, amorphous substance readily soluble in water. It is obtained from the bark of trees and from gall-nuts. Tannin is extensively used in the process of *tanning*. This consists in dipping the skin of an animal in a solution of tannin; the skin becomes much tougher, forming a compound with the tannin which constitutes *leather*. Tannin possesses the property of forming insoluble coloured compounds with many dye stuffs, and is therefore largely employed as a mordant. A third important application of tannin is in the manufacture of ink; this is obtained as a deep blue solution on adding ferric chloride to an aqueous solution of tannin. This reaction serves as a test for tannin.

**471. Solvent Naphtha, or Burning Naphtha,** is a colourless liquid consisting of a mixture of hydrocarbons—xylene, etc., and is obtained from coal-tar. It constitutes the fraction of coal-tar which boils between  $140^\circ C.$  and  $170^\circ C.$

**Creosote Oil** is that fraction of coal-tar which boils between  $230^\circ C.$  and  $270^\circ C.$  It consists of a mixture of carbolic acid, cresol (a substance closely resembling carbolic acid), naphthalene, and anthracene. It is largely employed for preserving timber, *e.g.* the sleepers on railways, on account of its antiseptic properties.

\* These three bodies, carbolic acid, hydroquinone, and pyrogallol, are all closely related to benzene. They are, in fact, hydroxy-benzenes, and their constitutional formulæ are as follows, benzene being given also for the purpose of comparison—

	Benzene	
Carbolic acid	$C_6H_5(OH)$	$C_6H_5(H)$
Hydroquinone	$C_6H_4(OH)_2$	$C_6H_4(H)_2$
Pyrogallol	$C_6H_3(OH)_3$	$C_6H_3(H)_3$

## QUESTIONS.—CHAPTER XXXIII.

## SECTION I.

1. Give an account of the preparation of pure alcohol from grape sugar. Give experiments which show that it may be considered to be a base.
2. Describe the process by which *beer* is manufactured.
3. Describe the more important reactions between alcohol and sulphuric acid, and compare the products.
4. State the chief physical and chemical properties of alcohol.

## SECTION II

1. Describe a method of oxidising alcohol and separating acetic acid from the product.
2. Describe the preparation of *pure* acetic acid from the acid obtained by the destructive distillation of wood.
3. How is vinegar manufactured? How would you prove that vinegar contains the same acid as that prepared by the oxidation of alcohol?
4. Write a short account of the properties of acetic acid.
5. Describe the preparation of oxalic acid from salt of sorrel. What is the action of sulphuric acid on oxalic acid?
6. How is oxalic acid manufactured? How would you prove experimentally that it is a dibasic acid?
7. Write a short account of the salts of acetic and oxalic acids.
8. In what forms do oxalic and tartaric acids occur in nature? For what purposes are these acids employed?
9. What is argol? How would you proceed to prepare tartaric acid from it?



10. How is tartaric acid manufactured? What experiments would you perform in order to find its basicity, and what result would you arrive at?
11. What happens when tartaric acid is (1) heated with strong sulphuric acid; (2) added to a strong solution of a potassium salt? What are *Rockelle salt* and cream of tartar?

## SECTION III.

1. What is benzene? Give some account of its properties and uses. How does it differ from benzine?
2. Indicate briefly the properties and uses of carbolic acid, creosote oil, and tannin.

## ANSWERS TO QUESTIONS.

- Chap. xiii. 3 2 vols. of hydrogen  
 „ 6. 11 205 grammes of hydrogen  
               88·795 grammes of oxygen.  
 „ 9. 1 61° C.  
 „ 10. 3 195° C.  
 „ 12. 41 3 grms.  
 „ 13 1000, 33, 63600.  
 „ 16. 19 95, 127·5.  
 „ 17 449·75, 44·975, 1349·25.  
               225 25, 22·525, 675·75  
 „ 18. 44·975 of CO<sub>2</sub> and 19·475 of O<sub>2</sub>.  
 Chap. xvi. 6. 19·6.  
 „ 7. 78·49, 0·68, 20·83.  
 „ 8. 22 97.  
 Chap. xix. 2. 5660 c.c.  
 Chap. xx. 21. Disodium hydrogen phosphate, Na<sub>2</sub>HPO<sub>4</sub>.  
               88·75 grms.  
 Chap. xxi. 2. 4399 tons.  
 „ 22. 0·57 per cent.  
 „ 23. 1146·7 c.c.  
 „ 24. 30 c.c. 20 c.c.  
 „ 25. 60 c.c. of oxygen.  
 „ 26. 85 c.c.  
               55 c.c. of oxygen, 20 c.c. of carbon  
               dioxide; 10 c.c. of water vapour.  
 Chap. xxii. 13. 8550 c.c., 2020 c.c.

# ANSWERS TO CHEMICAL CALCULATIONS IN CHAPTER XXVII.

1.  $91^{\circ}$ .
2. 293 : 253.
3. 50 c.c., 90.9 c.c., 140.9 c.c.
4. 2090 c.c., 418 c.c., 104.5 c.c., 38 c.c.
5. 441 c.c.
6. 129.7 c.c.
7. 488 mm.
8.  $273^{\circ}$  C.
9. 3,947 atmospheres.
10. 6,888 atmospheres.
11. 571.4 c.c.
12. 152.2 grammes; 65.7 c.c.
13. 73.9 c.c.; 180.4 grammes.
14. Ca = 40 per cent.  
O = 12 „  
O = 48 „  
44 per cent.
15. H = 7.44 per cent.  
Cl = 33.02 „  
O = 59.54 „
16.  $\text{FeS}_2$
17.  $\text{Fe}_3\text{O}_4$ .
18.  $\text{Na}_3\text{P}_4\text{O}_{18}$ .
19. 465.7 grammes.
20. 81.8 cc.
21. 4.852 grammes.
22. 17.91 litres.
23. 2.446 grammes.
24. 72 litres; 142.6 grms.
25. Oxygen, 23; Oxygen, 20.7.  
Nitrogen, 77; Nitrogen, 79.3.
26. Hydrogen, 11.1.  
Oxygen, 88.9.
27. 4.622 litres.
28. (a) N = 7.5 c.c.  
H = 22.5 c.c.  
O = 40.0 c.c.  
(b) N = 7.5 c.c.  
O = 28.75 c.c.
29. Oxygen = 3.73 c.c.  
Carbon dioxide = 16.36 c.c.
30. Oxygen = 0.37 c.c.  
Carbon dioxide = 163.6 c.c.
31. 3.534 per cent.
32. 61.023; 28.317.
33. 42.1 per cent.  
0.157 litre.
34. 180 c.c.; 140 c.c.
35. 14.18 grammes.
36. 100 c.c.; 0.072 gramme.
37. 29 per cent.
38. 252.0 kilogrammes.
39. Nitrogen, 79.00 per cent.  
Oxygen, 18.88 „  
Carbon } 2.12 „  
dioxide, }

# APPENDIX I.

## THE METRIC SYSTEM OF WEIGHTS AND MEASURES.

THE metric system has been found the most convenient for operations in which weighing and measuring are concerned, and it is universally used in scientific work.

The *unit of length* in this system is the *metre*, which is equivalent to 39 37 inches.

The *unit of volume* is that of a cube whose side is  $\frac{1}{100}$  of a metre, equivalent to very nearly one-sixteenth of a cubic inch, and the *unit of weight* is the weight of this volume of water, the temperature being that at which water has its maximum density, viz. 4° C. This weight is termed the *gramme*, and is equivalent to 15 432 grains.

The prefix *kilo* indicates the multiple 1,000, thus—

$$1 \text{ kilogramme} = 1,000 \text{ grammes} = 15,432 \text{ grains} = \text{about } 2 \frac{2}{3} \text{ lbs.}$$

The prefixes *deci*, *centi*, and *milla* respectively indicate the fractional parts  $\frac{1}{10}$ ,  $\frac{1}{100}$  and  $\frac{1}{1000}$ .

$$1 \text{ decimetre} = \frac{1}{10} \text{ metre} = 3 \frac{937}{1000} \text{ inches.}$$

$$1 \text{ centimetre} = \frac{1}{100} \text{ " } = 0 \cdot 3937 \text{ "}$$

$$1 \text{ millimetre} = \frac{1}{1000} \text{ " } = 0 \cdot 03937 \text{ "}$$

One inch is thus slightly more than 25 millimetres.

$$1 \text{ decigramme} = \frac{1}{10} \text{ gramme} = 1 \cdot 5432 \text{ grains.}$$

$$1 \text{ centigramme} = \frac{1}{100} \text{ " } = 0 \cdot 15432 \text{ "}$$

$$1 \text{ milligramme} = \frac{1}{1000} \text{ " } = 0 \cdot 015432 \text{ "}$$

A measure of volume very frequently employed is the *litre*, which is the volume occupied by a kilogramme of water at 4° C., it is therefore equivalent to a cubic decimetre, or, in English measure, 61 027 cubic inches.

## APPENDIX II.

### TABLES FOR REDUCTION OF MOIST GAS TO STANDARD CONDITIONS.

THE volume of a moist gas having been measured at a given temperature and pressure it is necessary to first find what volume the *dry* gas would occupy at 0° C. and 760 mm. pressure. Allowance must be made (see Chaps. VIII, XIII)—

- (a) for the temperature of the gas (*i e.* of the room) ;
- (b) for the pressure to which it is subject (that of the atmosphere at the time of the experiment) ;
- (c) the tension of water-vapour.

This involves a somewhat complex calculation, and a table has therefore been drawn up to enable the student to make the correction by using the factor given in the table.

Thus suppose the temperature of the laboratory to be 10° C. and the atmospheric pressure 740 m m. ; the tension of aqueous vapour with which the gas is saturated is for 10° C., 9.1 mm. Now if  $v$  is the volume of the moist gas as observed, then  $V$  the volume of the dry gas at 0° C. and 760 mm. pressure is given by the expression—

$$V = \frac{v \times 273 \times (740 - 9.1)}{283 \times 760} = 0.928 v.$$

To deduce the volume of the dry gas at standard temperature and pressure from the observed volume it is therefore only necessary to *multiply this latter by the factor* 0.928 as taken from the table, and so for any other temperature or pressure.

	10° C.	12° C.	14° C.	16° C.	18° C.	20° C.
Pressure.						
730 mm.	0·915	0·907	0·899	0·891	0·882	0·874
740 mm.	0·928	0·920	0·911	0·903	0·895	0·886
750 mm.	0·940	0·932	0·924	0·915	0·907	0·898
760 mm.	0·953	0·945	0·936	0·928	0·919	0·910
770 mm.	0·966	0·957	0·949	0·940	0·932	0·923

For intermediate temperatures or pressures, the value may be expressed with sufficient accuracy by taking the proportional mean; *e. g.* for 10° C. and 745 mm. we shall find 0·934, and for 11° C. and 750 mm. we shall find 0·936.

If we desire to know the *weight* of the hydrogen liberated, the following table may be used. Taking the weight of a litre of dry hydrogen under standard conditions as 0·09 gramme the table gives the weight of hydrogen in a litre of the moist gas collected at the temperature and pressure given.

	10° C.	12° C.	14° C.	16° C.	18° C.	20° C.
Pressure.						
730 mm.	0·0824	0·0816	0·0809	0·0802	0·0794	0·0787
740 mm.	0·0835	0·0828	0·0820	0·0813	0·0806	0·0798
750 mm.	0·0846	0·0839	0·0832	0·0824	0·0816	0·0808
760 mm.	0·0858	0·0851	0·0843	0·0835	0·0827	0·0820
770 mm.	0·0869	0·0861	0·0854	0·0846	0·0839	0·0831

An example will make the method of using the table quite clear:—

Thermometer 16° C.  
Barometer 750 mm.

Observed volume of gas, 120 c.c.

The factor under 16° C. and 750 mm. is 0·0824.

$$\text{Weight of hydrogen} = \frac{0\cdot0824 \times 120}{1,000} = 0\cdot00988 \text{ gramme.}$$

## APPENDIX III.

### SUBSTANCES IN COMMON USE IN THE LABORATORY.

**Asbestos** is a white fibrous variety of the mineral hornblende, which consists of calcium, magnesium and iron (ferrous) silicates.

**Fehling's Solution** is prepared by dissolving copper sulphate and Rochelle salt in water and then adding caustic soda to render the solution alkaline.

**Litmus** is a blue colouring matter which occurs in certain lichens such as *Rocella* and *Varolaria*. The colour is changed to red by acids, but is restored by alkalies.

**Microcosmic Salt** is sodium ammonium hydrogen phosphate,  $\text{NaNH}_4\text{HPO}_4$ . It is a colourless salt prepared by the action of ammonium chloride on common sodium phosphate.

**Nessler's Reagent** is prepared by adding potassium iodide solution to mercuric chloride till the precipitate of mercuric iodide first formed just dissolves in excess of the potassium iodide (forming the soluble compound  $\text{HgI}_2 \cdot 2\text{KI}$ ), and then rendering the solution alkaline by the addition of caustic potash.

**Turmeric** is the root of a plant found in the East Indies. It contains a yellow colouring matter which is turned brown by acids.

## APPENDIX IV.

### COMMON POISONS AND THEIR ANTIDOTES.

In choosing an antidote for a poison, the object is generally to find some substance which will form an insoluble compound with the poison and so prevent its absorption into the system. For example, in case of lead

poisoning, a soluble sulphate such as alum or Glauber's salt should be administered, this results in the formation of insoluble lead sulphate. In the case of strong acids, however, the free acids must be neutralised, so such substances as washing soda or magnesia are used, though the compounds produced are soluble

The following is a list of the poisons commonly met with, and the antidotes usually employed for each of them :—

Poison.	Antidotes.
Hydrochloric acid . .	Magnesia and water, or washing soda.
Sulphuric acid . .	" "
Nitric acid . .	" "
Oxalic acid . .	Chalk and water (insoluble calcium oxalate formed).
Salt of sorrel (or lemon)	" "
Prussic acid . .	Ferrous sulphate, ferric chloride and washing soda Insoluble Prussian blue is formed. Magnesia may be used instead of washing soda
Arsenic compounds .	Ferric hydroxide (insoluble ferrous arsenate formed).
Antimony compounds .	Tannic acid (infusion of tea) or ferric hydroxide.
Mercury compounds ( <i>e g</i> corrosive sublimate)	White of egg.
Lead compounds . .	Glauber's salt, Epsom salts or alum (insoluble lead sulphate formed).
Barium compounds .	Glauber's salt, Epsom salts or alum (insoluble barium sulphate formed)
Copper compounds .	White of egg, potassium ferrocyanide (insoluble copper ferrocyanide formed), or iron filings (copper precipitated in the metallic state).
Zinc compounds . .	Washing soda followed by white of egg.
Tin compounds . .	White of egg, or ammonium carbonate.
Strychnine . .	Tannic acid (infusion of tea).
Morphine . .	" "
Opium . .	" "
Laudanum . .	" "



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